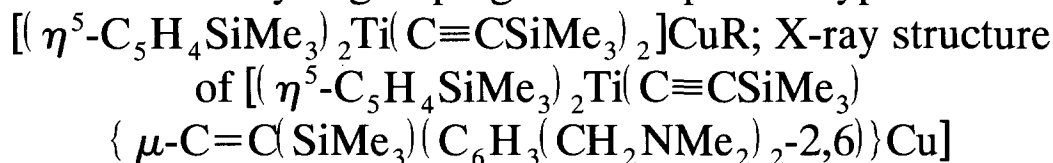Preliminary communication

Intramolecular addition of monomeric arylcopper entities across an alkyne grouping in a complex of type $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]CuR$; X-ray structure of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)\{\mu\text{-}C=C(SiMe_3)(C_6H_3(CH_2NMe_2)_2\text{-}2,6)\}Cu]$

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Abstract

The tetranuclear heteroleptic arylcopper aggregate $[Cu_4R_2Br_2]$ (R = $C_6H_3(CH_2NMe_2)_2\text{-}2,6$) reacts with the organometallic 1,4-diyne $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]$, **1**, to give equivalent amounts of known $[1 \cdot CuBr]$, and the novel 1,1-*bis*-metalla alkenyl complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)\{\mu\text{-}C=C(SiMe_3)(R)\}Cu]$, **6**, that is the result of intramolecular addition of a Cu–C bond across the alkyne triple bond.

Keywords: Alkenylcopper; Arylcopper; Intramolecular addition; Alkynes; *bis*-metalla alkenyl; bis(alkynyl)titanocene

Recently, we have reported that monomeric Cu^{I}R entities (R = alkynyl [1] or aryl [2]) can be stabilized by using the chelating effect of the organometallic 1,4-diyne $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]$ (**1**) [3] in the form of $[1 \cdot MR]$. In the latter species both alkyne groups coordinate in an η^2-fashion to the copper or silver atom, which is additionally η^1-bonded to the ligand R, resulting in a trigonal planar environment of the group 11 metal centre. The stability of the complexes $[1 \cdot CuR]$ (R = alkynyl [1], or aryl [2]) is strongly dependent on the nature of R and we have already reported that alkynylcopper complexes $[1 \cdot CuC\equiv CR]$ undergo nucleophilic substitution of one of the trimethylsilyl groups of the $Ti(C\equiv CSiMe_3)_2$ entity to afford species with a Ti–C≡C–Cu entity [1].

In ongoing studies we have isolated and characterized arylcopper complexes $[1 \cdot CuR]$ (R = $C_6H_2Me_3$-2,4,6 (**5a**) [2], C_6H_4Me-4 (**5b**), C_6H_4OMe-4 (**5c**), $C_6H_4NMe_2$-4 (**5d**), C_6H_5 (**5e**)) [4] in which the aryl group has either Me or H substituents in the ortho-position. During these studies we have now found that attempted preparation of the analogue where R is $C_6H_3(CH_2NMe_2)_2$-2,6 does not lead to the expected species $[1 \cdot Cu\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, **5f**, but instead to an unusual isomeric complex with a unique $Ti\{\mu:\eta^1\text{-}C=C(SiMe_3)(R)\}Cu$ unit. The synthesis and structural characterization of this 1,1-*bis*-metalla alkenyl species are the subject of this communication and a probable mechanism for its formation by an intramolecular rearrangement of **5f** is outlined.

Reaction of **1** with $[Cu_4R_2Br_2]$ (R = $C_6H_3(CH_2NMe_2)_2$-2,6), **2** [5], in a 4:1 molar ratio in Et_2O at 25°C results in the clean formation of a unique species characterized as $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)\{\mu\text{-}C=C(SiMe_3)(R)\}Cu]$, **6**, [6] and known
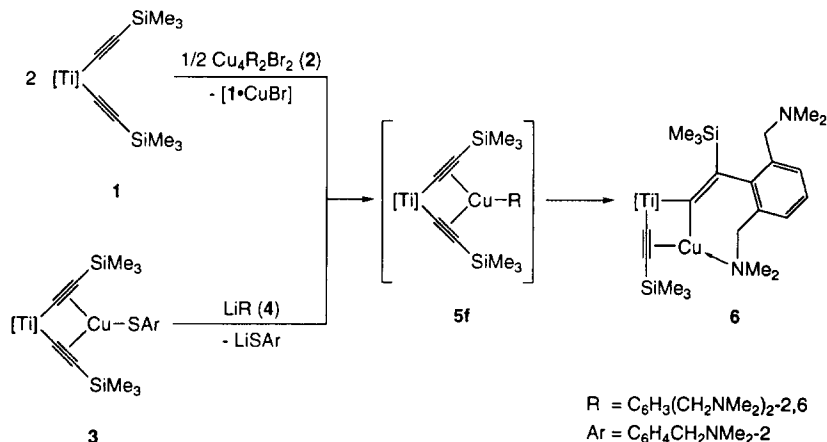
Scheme 1. Synthesis of the 1,1-*bis*-metalla alkenyl complex **6**; $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$ is abbreviated as [Ti].

[**1** · CuBr] [7] (Scheme 1). After removal of the volatiles from the reaction mixture, complex **6** can be extracted with pentane (in which [**1** · CuBr] is not soluble), and further work-up and recrystallization from Et_2O at $-20°C$ affords **6** in 86% yield as orange to red crystals which are stable in air for several hours. Complex **6** is soluble in most organic solvents to afford solutions which exhibit significant decomposition after exposure to air for 1 h.

An alternative and also virtually quantitative synthesis of **6** comprises the 2:1 molar reaction of the monomeric copper arenethiolate complex [**1** · $CuSC_6H_4CH_2NMe_2$-2], **3** [7], with [$LiC_6H_3(CH_2NMe_2)_2$-2,6]$_2$, **4** [8]. A similar work-up procedure to that already described can provide **6** in 97% yield.

To assist in the identification of **6**, a single crystal X-ray structure determination of this complex has been carried out [9]. The crystal structure shows the unit cell to contain two crystallographically independent, but chemically identical, heterobimetallic molecules [(η^5-$C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)\{ \mu$-C=C(SiMe$_3$)($C_6H_3$-$(CH_2NMe_2)_2$-2,6)\}Cu] and Fig. 1 shows one of these molecules together with the adopted atom numbering scheme.

Each molecule of **6** contains a (η^5-$C_5H_4SiMe_3)_2$ Ti unit that is η^1-bonded to the terminal carbon atom of a $C\equiv CSiMe_3$ group and of a $C=C(SiMe_3)(C_6H_3(CH_2 NMe_2)_2$-2,6) grouping which, through being also η^1-C-bonded to a copper atom, is present as a bridging 1,1-*bis*-metalla alkenyl unit. Within this 1,1-*bis*-metalla
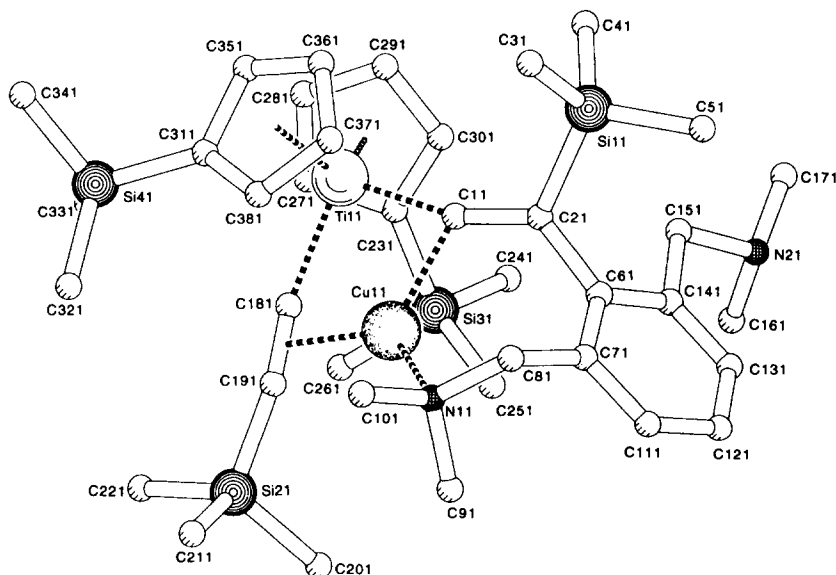

Fig. 1. PLUTON drawing of one of the two crystallographically independent residues of **6** with the exclusion of the hydrogen atoms and with the adopted atom labelling scheme. Selected bond distances (Å) and bond angles (°) [the bond lengths and angles in square brackets are for the equivalent bonds in the other residue]. Ti11...Cu11 2.639(4) [2.635(4)], Cu11–C11 2.031(14) [2.042(16)], Cu11–C181 1.972(16) [1.967(15)], Cu11–C191 2.236(18) [2.209(16)], Cu11–N11 2.027(12) [1.996(13)], C11–C21 1.357(19) [1.35(2)], C181–C191 1.24(2) [1.24(2)], Ti11–C11 2.044(14) [2.026(15)], Ti11–C181 2.153(16) [2.149(16)]; Cu11–C11–Ti11 80.7(5) [80.8(6)], Ti11–C11–C21 160.6(11) [163.0(13)], Cu11–C11–C21 117.6(10) [115.8(12)], Ti11–C181–C191 163.7(14) [163.2(13)], C181–C191–Si21 163.1(16) [161.4(14)], C11–Ti11–C181 95.8(6) [96.1(6)].

alkenyl bridge the bond lengths of the metal to bridging carbon atom (C11) are 2.044(14) Å for Ti11–C11 and 2.031(14) Å for Cu11–C11. The C11–C21 bond length of the 1,1-*bis*-metalla alkenyl function amounts to 1.357(19) Å, compatible with this being a C=C double bond; it is significantly longer than the 1.24(2) Å bond length of the C181–C191 triple bond of the C≡CSiMe$_3$ ligand.

The copper atom in **6** attains a trigonal planar geometry through additional η^2-bonding to the C≡CSiMe$_3$ group and coordination of the N-donor atom (N11) of one of the ortho (dimethylamino)methyl substituents on the aryl ring of the C=C(SiMe$_3$)(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6) grouping, whereby a 7-membered chelate ring, Cu11–C11–C21–C61–C71–C81–N11, is formed; the second CH$_2$NMe$_2$ group does not coordinate. Probably as a result of strain in the 7-membered chelate ring there is a slightly distorted trigonal planar geometry of the copper atoms (sum of the angles is 356.6°) which is illustrated by the angles C11–Cu11–N11, N11–Cu11–mid1, and mid1–Cu11–C11 of 109.0(5), 127.7(6), and 119.9(6)°, respectively (mid1 is defined as the midpoint of C181–C191). The Cu11–C11–Ti11 bridge angle of 80.7(5)° in **6** is acute and the plane of the μ-C=C(SiMe$_3$)(R) alkenyl unit is tilted 23.3(8)° with respect to the Ti–C11–Cu plane. Similar features are present in several 1,1-bimetalla alkene complexes and reported M–C–M angles (M = transition metal) are in the range of 82.3 to 90.0° [10].

The tilting of the μ-C=C(SiMe$_3$)(R) entity with respect to the Ti–C11–Cu plane is likely to result from steric hindrance of the alkene SiMe$_3$ group with one of the η^5-C$_5$H$_4$SiMe$_3$ ligands. The positioning of the trigonal copper atom and the alkene moiety is consistent with a σ-bond between Cu11 and C11 (Cu11–C11–C21 is 117.6(10)°), while the angle Ti11–C11–C21 of 160.6(11)° indicates that the Ti11–C11 interaction may be best described as a bent bond in which the orbitals involved are positioned outside the Ti11–C11–Cu11 triangle. Similar bonding schemes were obtained from Extended Hückel calculations on μ-methylene transition metal compounds where the bonding is referred to as similar to the Walsh-orbitals for cyclopropane [11].

The low temperature ^{1}H NMR spectrum (237 K) of **6** consists of three different aryl protons, seven singlets for the C$_5$H$_4$ protons (ratio 1:1:1:1:1:1:2), one AB pattern and one singlet for the benzylic protons, three singlets (ratio 2:1:1) for the dimethylamino protons and four singlets for the SiMe$_3$ protons. This is consistent with an asymmetric molecule, as is found in the solid state structure (Fig. 1).

Complex **6** is unique as it is the first mononuclear alkenylcopper species as well as the first example of a 1-metalla-1-copper alkene species; in the literature there are only two other structurally characterized alkenylcopper compounds, i.e. [Cu$_4${(4-MeC$_6$H$_4$)-(Me)C=C-

(C$_6$H$_4$NMe$_2$-2)}$_2$(R)$_2$] (R = C$_6$H$_4$NMe$_2$-2, Br) [12]. Complex **6** can be clearly seen as the result of a formal addition of a Cu–R (R = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6) moiety across a TiC≡CSiMe$_3$ unit. This type of reaction of organocopper reagents is a well described reaction in organic synthesis [13].

In the synthesis of **6**, either by reaction of **1** with **2** or by reaction of **3** with **4**, it is likely that the coordination complex [**1** · Cu(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6)], **5f**, is formed as intermediate, since the arylcopper complexes **5a–5e** could be prepared by similar synthetic procedures [1, 2, 3]. However, in the course of this study the intermediate coordination complex **5f** could not be identified. Moreover, the bis(η^2-alkyne)copper(η^1-mesityl) complex [**1** · Cu{η^1-C$_6$H$_2$Me$_3$-2,4,6}], **5a**, without coordinating ortho-substituents, is stable in the solid state up to 124°C [2], whereas the complexes [**1** · CuR] (R = C$_6$H$_4$Me-4) (**5b**), C$_6$H$_4$OMe-4 (**5c**), C$_6$H$_4$NMe$_2$-4 (**5d**), C$_6$H$_5$ (**5e**)) [4] which completely lack ortho-substituents rearrange in solution at temperatures around 0°C to afford the corresponding addition products [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$){ μ-(C=C(SiMe$_3$)(R)}Cu]. To help identify the latter unstable addition products, benzene solutions of **5b–5e** were heated for 1 h at reflux, followed by acidic hydrolysis and GC-MS analysis of the resulting volatiles. From these experiments the alkyne HC≡CSiMe$_3$ (resulting from the intact TiC≡CSiMe$_3$ moiety), the alkene H$_2$C=C(SiMe$_3$)(R) (from the Ti{ μ-C=C(SiMe$_3$)(R)}Cu entity), and trimethylsilyl-cyclopentadiene were identified as the major organic products. Both the isolation of complexes **5b–5e** below 0°C and the observed addition reaction in **5b–5e** [4], suggests that the addition reaction proceeds intramolecularly within the pre-formed species [**1** · CuR]. The intramolecular coordination of the (dimethylamino)methyl substituents in complex **6** is crucial for its isolation, since absence of this coordination (i.e. in complexes **5b–5e**) merely leads to decomposition of the corresponding addition products.

It has been shown that the use of the organometallic 1,4-diyne, **1**, yields monomeric organocopper species [**1** · CuR] which can be studied in detail, but when combined with the organic diarylamine ligand C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6 also gives access to a novel class of alkenylcopper compounds. Our studies on species [**1** · CuR] in this way form a practical and unique way of investigating the reactivity profile of mononuclear entities CuR and we have already established that both addition (R = aryl) and substitution (R = alkynyl) pathways may be encountered.

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[6] To [Cu$_4$(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6)$_2$Br$_2$] (2) (0.38 g, 0.48 mmol of Cu$_4$ aggregate) in Et$_2$O (50 ml) was added in one portion 1 (0.99 g, 1.92 mmol) at 25°C. The reaction mixture gradually turned deep-red and after stirring for 3 h all volatiles were evaporated in vacuo. Extraction with pentane (three times 40 ml) and subsequent evaporation of the volatiles in vacuo yielded 0.64 g (86%, 0.83 mmol) of 6: mp 138°C (dec); IR(KBr) v/cm^{-1} 1882 (C≡C), 1591 (C=C); ^{1}H NMR (300.13 MHz, C$_6$D$_5$CD$_3$, 237 K), δ 0.15 (s, 9H, SiMe$_3$), 0.27 (s, 9H, SiMe$_3$), 0.34 (s, 9H, SiMe$_3$), 0.48 (s, 9H, SiMe$_3$), 2.10 (s, 3H, NMe$_2$), 2.20 (s, 3H, NMe$_2$), 2.44 (s, 6H, NMe$_2$), 2.50 (d, 1H, $^2J = 10$ Hz, CH$_2$), 3.91 (s, 2H, CH$_2$), 4.11 (d, 1H, $^2J = 10$ Hz, CH$_2$), 5.21 (br s, 2H, C$_5$H$_4$), 5.27 (br s, 1H, C$_5$H$_4$), 5.34 (br s, 1H, C$_5$H$_4$), 5.45 (br s, 1H, C$_5$H$_4$), 5.82 (br s, 1H, C$_5$H$_4$), 6.05 (br s, 1H, C$_5$H$_4$), 6.17 (br s, 1H, C$_5$H$_4$), 6.79 (d, 1H, $^3J = 7$ Hz, ArH), 7.13 (m, 1H, ArH), 8.02 (d, 1H, $^3J = 8$ Hz, ArH).

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[9] Single crystals of 6 were obtained by cooling a saturated Et$_2$O solution to −20°C. Crystal data for 6: C$_{38}$H$_{63}$N$_2$Si$_4$CuTi, $M_r = 771.70$, orange needle-shaped crystal (1.0×0.10×0.05 mm), monoclinic, space group $P2_1$/c, with $a = 31.05(2)$ Å,

$b = 14.323(3)$ Å, $c = 20.014(8)$ Å, $\beta = 108.53(5)°$, $V = 8440(7)$ Å^3, $Z = 8$, $d_{calc} = 1.215(1)$ g cm^{-3}, $F(000) = 3296$, μ(Mo Kα) $= 8.3$ cm^{-1}, 15988 reflections ($0.69 < \theta < 25.00°$; $\omega/2\theta$ scan; $T = 150$ K) were measured on an Enraf-Nonius CAD-4T Rotating Anode diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz-Polarization effects and for a linear decay (0.2%) of the intensity control reflections and merged into a dataset of 12882 unique reflections. The structure was solved with Direct Methods (SHELXS86) and difference Fourier techniques. The crystal is pseudo-merohedrally twinned by a twofold axis coinciding with a^*. The twinning was taken into account using the TWIN option of the SHELXL93 program, resulting in a twin-ratio of 0.325(3): 0.675(3). Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. In view of the twinning and the related limited quality of the data, only the Cu, Ti, and Si atoms were refined with anisotropic atomic displacement parameters, all other non-hydrogen atoms were refined with individual isotropic atomic displacement parameters. Refinement on F^2 (SHELXL93) using all 12882 unique reflections converged at $R_1 = 0.1233$ for 8564 reflections with $I > 2.0$ $\sigma(I)$ and 462 parameters; $wR_2 = 0.3432$, $S = 1.033$ for all 12882 reflections, $w = 1/[\sigma^2(F^2)+(0.2281P)^2]$. A final difference Fourier map shows residual density in the range -1.37: 3.31 e Å^{-3} (probably a residual twinning effect). The structure contains some solvent accessible voids of about 35 Å^3; no residual electron densities were found in these areas (PLATON-SQUEEZE). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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