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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF THE POLYNUCLEAR ORGANOCOPPER—COPPER HALIDE COMPOUND $[(4\text{-MeC}_6H_4)\text{MeC=C}(C_6H_4\text{NMe}_2\text{-2})]_2\text{Cu}_4\text{Br}_2$ CONTAINING BRIDGING VINYL GROUPS

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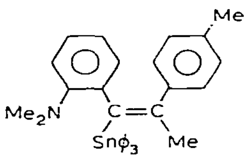
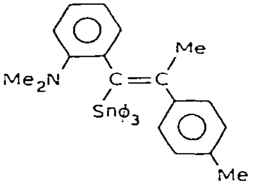
Summary

The isolation and the hydrolytic, thermal and oxidative decomposition of a stable organocopper compound, $\text{Vi}_2\text{Cu}_4\text{Br}_2$, containing 2*e*—3*c* bonded vinyl ligands, is described.

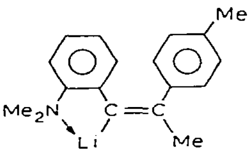
Recently obtained structural information on various types of organocopper compounds, e.g. $R_4\text{Cu}_4$ (R = $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$ [1] or Me_3SiCH_2 [2]) and $R'_4\text{Cu}_6X_2$ (R' = $2\text{-Me}_2\text{NC}_6\text{H}_4$, X = Br [3], C≡CAr [4] or OTf [5]), has improved understanding of the reactivity of organocopper compounds useful in organic synthesis (see e.g. ref. 6 and 7). In spite of their growing importance as synthetic intermediates [8—10], vinylcopper compounds have not been isolated in the pure state and no structural information on them is available. We have found that intramolecular coordination and/or steric crowding near the Cu_2C 2*e*—3*c* bond enhances the stability of organocopper compounds. This principle has now been applied to the isolation of a pure vinylcopper compound.



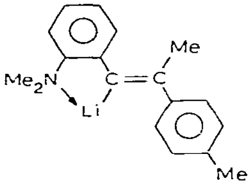
(E-I)



(Z-I)



(Z-II)



(E-II)

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The 1/1 reaction of n-BuLi with the organotin compound *E*-ViPh$_3$Sn* (*E*-I, Vi = [1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)propen-1-yl], m.p. 177°C) in pentane proceeds with retention of configuration to give the pentane-insoluble *Z*-ViLi (*Z*-II).

Dissolution of *Z*-II in benzene or ether results in quantitative inversion of configuration affording *E*-ViLi [*E*-II: dimeric (Vi$_2$Li$_2$) in benzene (cryosc.)].

Reaction of *E*-II with Ph$_3$SnCl gives *Z*-ViPh$_3$Sn (*Z*-I, 30% yield, m.p. 129°C) with retention of configuration.

The configuration of *E*-I, *Z*-I, *E*-II and *Z*-II has been unambiguously established by the values of $^3J(^{119}\text{Sn}—^{13}\text{C})$ (*E*-I: 48 Hz; *Z*-I: 58 Hz) and of $^3J(^1\text{H}—^{13}\text{C})$ of the hydrolysis products of II. [Hydrolysis of *E*-II and *Z*-II occurs with retention of configuration: *Z*-ViH (*Z*-III): 7.5 Hz; *E*-ViH (*E*-III): 8.6 Hz]**.

Addition of *E*-ViLi (*E*-II) to an ether suspension of 2 equivalents of CuBr at 0°C afforded in 50% yield a yellow crystalline product which according to the elemental analysis is a 1/1 complex of ViCu and CuBr (IV). IV shows high thermal stability (dec. 155°C). Molecular weight determination in benzene revealed a Vi$_2$Cu$_4$Br$_2$ stoichiometry (cryosc., found: 905; calcd. 905, conc. independent).

DNMR spectroscopy (toluene-d_8) reveals only one resonance pattern for the NMe$_2$ (2.43 ppm), C=CMe (2.10 ppm) and C$_6$H$_4$Me-4 (2.25 ppm) methyl protons, pointing to a symmetrical arrangement of the Vi groups. At 25°C the NMe groups are isochronous. Below 0°C two singlets (2.54 and 2.22 ppm, *T*(coalesc.) 20°C) are observed, which points to diastereotopic NMe groups. The proposed structure (Fig. 1) with bridging vinyl groups*** and Cu—N coordination resulting in a five-membered chelate ring (cf. ref. 1) accounts for these observations. The bridging vinyl carbon atom is a chiral

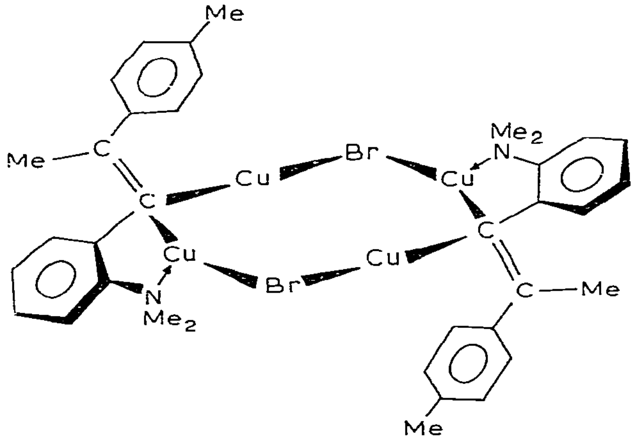

Fig.1. Proposed structure of Vi$_2$Cu$_4$Br$_2$ (*Z*-IV).

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*[*] *E*-I was prepared by the nickel catalyzed addition [14] of MeMgBr to *N*,*N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine [7] followed by reaction with Ph$_3$SnCl.

**E.g., *trans*-α-methylstilbene: $^3J(^1\text{H}—^{13}\text{C})$: 8.3 Hz [15].

***The presence of a symmetrically bridging 2*e*-3c bonded vinyl ligand in (t-BuCHCH)$_2$(i-Bu)$_4$Al$_2$ has been confirmed by X-ray analysis [16].

centre because the bridged Cu atoms have different coordination symmetries (cf. ref. 11). Transmetallation reactions of vinyllithium reagents with metal halides occur with retention of configuration [12]. On this basis the aryl groups in Vi of IV are expected to be in *trans* positions (*Z*-ViCu)*.

That steric crowding in olefinic copper clusters is important can be deduced from the fact that the 1/1 reaction of ViLi with CuBr exclusively yields $Vi_2Cu_4Br_2$. Whereas the bromine atoms in $Vi_2Cu_4Br_2$ cannot be substituted by Vi, reaction with ArC≡CLi yields the vinyl-acetylide copper cluster $(ViCu_2C{\equiv}CAr)_n$.

Hydrolysis of benzene solutions of $Vi_2Cu_4Br_2$, which thus contains the Vi groups in only one configuration, is quantitative, and gives a mixture of *E*-ViH and *Z*-ViH in ratios depending on the type of reagent used [H_2O (70/30); MeOH (82/18); HCl/H_2O, 4N (86/14); HOAc (91/9); HCl/Et_2O (93/7); (*E*/*Z*)]. *E*-III and *Z*-III are configurationally stable in the presence of these reagents. These results are explained in terms of two different types of attack by the protonating reagents on the Cu_2C bond in $Vi_2Cu_4Br_2$; electrophilic attack of H^+ on the bridging C atom leads to an intermediate which can isomerize [13] to the sterically favoured conformation having the tolyl group and the bulky Cu_4 core in *trans* positions, whereas nucleophilic attack by the anion (e.g. HOAc) on copper followed by proton transfer and Cu_2C-bond breaking proceeds with retention.

Thermolysis of IV (benzene, 60°C) yields *E*-ViH and *Z*-ViH in a 3/2 ratio. Dimerization (formation of Vi—Vi) does not take place. Reaction of $Vi_2Cu_4Br_2$ with copper trifluoromethanesulfonate (CuOTf) (1/2.3 ratio) in benzene gives Vi—Vi (m/e: 500) quantitatively. This reaction must involve pairwise release of vinyl groups from a $(ViCu_2OTf)_n$** intermediate (cf. ref. 6). A compound with $ViCu_2OTf$ stoichiometry was synthesized by the 1/2 reaction of *E*-ViLi with CuOTf (V, white solid, dec. 135°C, slightly soluble in benzene). Thermolysis of V in benzene, which occurs even at 40°C, results in quantitative formation of Vi—Vi. The differing thermolysis behaviour of IV and V provide another example of the pronounced influence of the nature of the anionic group on the reactivity of mixed-cluster compounds $R_mCu_{m+n}X_n$.

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*The configuration of Vi in *E*-ViLi and *Z*-ViCu·CuBr is the same, because the *E*- and *Z*- conventional rules are based on atomic weights.

**OTf = triflate = trifluoromethanesulphonate.

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