GROUP IB ORGANOMETALLIC CHEMISTRY

XXXIV [*]. THERMAL BEHAVIOUR AND CHEMICAL REACTIVITY OF TETRANUCLEAR Me$_2$N-SUBSTITUTED DIARYLPROPENYLCOPPER-COPPER ANION (Vi$_2$Cu$_4$X$_2$) AND MIXED DIARYLPROPENYL/ORGANOCOPPER (Vi$_2$Cu$_4$R$_2$) COMPOUNDS [‡]

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Summary

Thermal decomposition of configurationally pure 1,2-diarylpropenylcopper compounds Z-Vi$_2$Cu$_4$Br$_2$ and Z-Vi$_2$Cu$_4$R$_2$ [Vi = (2-Me$_2$NC$_6$H$_4$)C=C(Me)-(C$_6$H$_4$Me-4), R = 2-Me$_2$NC$_6$H$_4$ or 4-MeC$_6$H$_4$C≡C] predominantly results in the formation of ViH. In contrast, only dimers (ViVi) were formed on thermolysis of (Z-ViCu$_2$OTf)$_n$ which is a further illustration of the influence of the counter anion on the reactivity of organocopper cluster compounds. However, in both cases partial inversion of configuration, giving mixtures of isomers, was observed. The thermolysis of (Z-ViCu$_2$OTf)$_n$ is discussed in terms of OTf-enhanced intraaggregate electron-transfer processes. The formation of incipient vinyl cations which are η^2-coordinated to the copper cluster can explain the observed isomerization.

Also in the hydrolysis reaction of Z-Vi$_2$Cu$_4$Br$_2$ mixtures of isomeric ViH compounds were obtained, the E/Z ratio being dependent on the type of reagent used. Mixtures of isomeric ViX compounds (X = Br, Cl, I) were formed in the reaction of Z-Vi$_2$Cu$_4$Br$_2$ with I$_2$ and CuCl$_2$. An explanation for the occurrence of isomerization is presented.

Dimers (ViVi) were almost absent in the product mixture resulting from the reaction of Z-Vi$_2$Cu$_4$Br$_2$ with CuCl$_2$. In contrast, ViVi is obtained in about 50% yield from the reaction of ViLi with CuCl$_2$ which is in accord with earlier observations for the reaction of aryllithium compounds with cupric halides.

Highly selective E-ViBr formation was observed in the reaction of E-ViLi with AgBr. This reaction probably proceeds via a thermally unstable Z-ViAg$_2$Br intermediate.

Introduction

The importance of in situ prepared alkenylcopper compounds and alkenyl-copperlithium compounds as reagents for the stereo- and regio-selective introduction of alkenyl groups in organic substrates is well established [2—5]. Detailed mechanistic studies of such reactions have been hampered by the lack of information about the exact nature of the intermediate alkenylcopper species. This is perhaps not surprisingly in view of the problems met in the isolation and characterization of pure alkenylcopper and alkenylcopperlithium compounds. Such compounds in general have low thermal stability and are extremely sensitive towards hydrolysis. E.g. 1-propenylcopper rapidly decomposes at 25°C even in the presence of PBu$_3$ [6].

In a recent publication we have described the striking enhancement of the thermal stability of propenylcopper compounds upon introduction of coordinating and/or bulky substituents in the propenyl moiety near the carbon— copper bond [7]. Substituted Z-1-propenylcopper—copper anion compounds [(ViCu · CuX)$_n$] which do not decompose below 100°C upon heating, were prepared via reaction of the corresponding E-1-propenyllithium compounds I and II (ViLi) * with copper(I) salts, eq. 1:

$$\text{(1)}$$
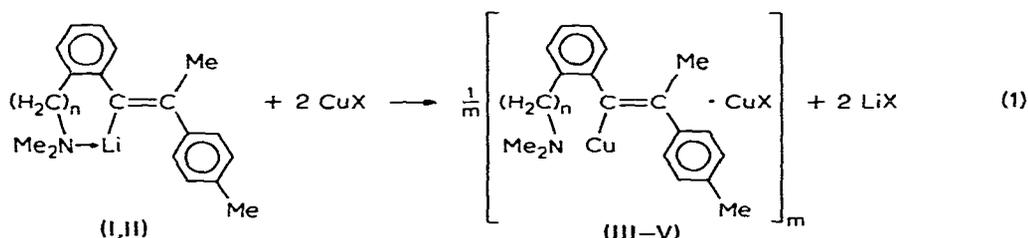
I. $n = 0$; II. $n = 1$; III. $n = 0$, X = Br, $m = 2$; IV. $n = 0$, X = OTf **, m = unknown; V. $n = 1$, X = Br, $m = 2$

Attempts to prepare the propenylcopper compounds (Z-ViCu) via the reaction of Z-Vi$_2$Cu$_4$Br$_2$ with excess of E-ViLi were unsuccessful: Substitution of the bromine atom in III via reaction of III with aryl- or alkynyllithium compounds afforded mixed-organocopper compounds of the type [(ViCu · CuR)$_n$], eq. 2.

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* The configuration of E-ViLi and Z-ViCu · CuBr are the same, because the E- and Z-configurations are based on atomic weights [8].

** OTf = trifluoromethanesulphonate = triflate.
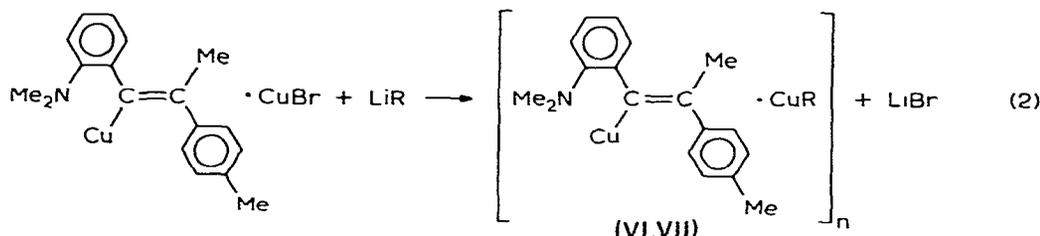
$$VI, R = C \equiv CC_6H_4Me\text{-}4, n = \text{unknown}; VII, R = C_6H_4NMe_2\text{-}2, n = 2$$

Compound VII, which is the first example of a tetranuclear mixed alkenyl/aryl-copper compound, has been fully characterized. As compared with 1-propenyl-copper, VII displays a remarkable thermal stability (dec. 225°C). A recently completed X-ray structure determination [9] revealed 3c-2e bridge bonding to the Cu$_4$ core for both the alkenyl and the aryl groups with the planes of these aryl and alkenyl ligands being oriented in a position perpendicular to the bridged Cu$_2$ pair. Furthermore, the edges of the planar Cu$_4$ core appeared to be occupied by the two types of ligands in a *cis*- rather than in a *trans*-arrangement (cf. ref. 7) (see Fig. 1).

The elucidation of the molecular structure of some arylcopper compounds, e.g. (5-Me-2-Me$_2$NCH$_2$C$_6$H$_3$)$_4$Cu$_4$ [10], (2-Me$_2$NC$_6$H$_4$)$_4$Cu$_6$Br$_2$ [11] and (2-Me$_2$NC$_6$H$_4$)$_4$Cu$_6$(C$\equiv$CC$_6$H$_4$Me-4)$_2$ [12] has given an important impetus to a better understanding of the mechanism of thermolysis reactions of arylcopper compounds. The polynuclearity of these structures together with the bridging nature of the aryl-to-copper bond nicely accounts for the highly selective biaryl formation on thermolysis of (2-Me$_2$NCH$_2$C$_6$H$_4$)$_4$Cu$_4$ [13] and (2-Me$_2$NC$_6$H$_4$)$_4$-Cu$_6$X$_2$ [14] in solution. The very selective asymmetric coupling reaction taking place on heating (2-Me$_2$NC$_6$H$_4$)$_4$Cu$_6$(C$\equiv$CC$_6$H$_4$Me-4)$_2$ in benzene, which gives exclusively 2-Me$_2$NC$_6$H$_4$C$\equiv$CC$_6$H$_4$Me-4, was interpreted on the basis of the unique arrangement of the organic ligands on four triangular faces of the Cu$_6$ octahedron present in this compound [15].

The availability of pure, configurationally stable alkenylcopper compounds as well as the availability of detailed structural information for one of these offers a good starting point for investigating the thermal behaviour as well as
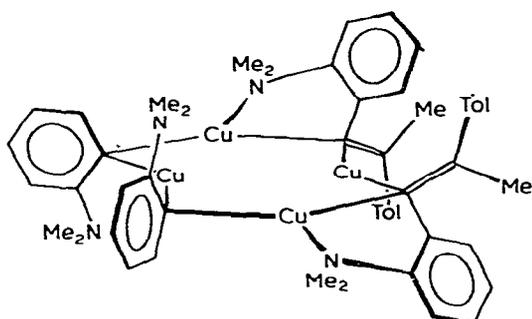

Fig. 1. Molecular structure of compound VII.

the chemical reactivity of propenylcopper compounds towards protolytic and halogenating reagents. In this paper we report the results of the thermolysis, hydrolysis and halogenation reactions exhibited by the propenylcopper derivatives. These results are compared with those obtained earlier for the polynuclear arylcopper cluster compounds mentioned above. Special attention has been paid to the elucidation of the stereochemistry of these reactions.

Results and discussion

Thermal behaviour

The thermal decomposition of the hexanuclear copper compounds $Ar_4Cu_6X_2$ (Ar = 2-$Me_2NC_6H_4$, X = Cl, I) which give ArAr in 90% yield [14] and of $Ar_4Cu_6(C{\equiv}CR')_2$ (Ar = 2-$Me_2NC_6H_4$, R' = 4-MeC_6H_4) which give $ArC{\equiv}CR'$ quantitatively [15], specifically results in C—C coupling. In contrast, thermal decomposition of the compounds Z-$Vi_2Cu_4Br_2$ (III) and Z-$Vi_2Cu_4R_2$ (VI and VII) in naphthalene at 220°C yields predominantly products ViH resulting from hydrogen abstraction. Mixtures of isomeric 1,2-diarylpropenes are obtained in high yield (III: E-ViH: 63%, Z-ViH: 27%; VI: E-ViH; 91%, Z-ViH: 4%; VII: E- and Z-ViH: 65%). Symmetric dimeric products (ViVi or RR) were not formed and only minor amounts of asymmetric coupling products ViR were detected in the thermolysis of VI (~5%) and VII (~20%).

The formation of H-abstraction products and the occurrence of stereoisomerization are surprising in view of the previous results reported for the thermolysis of alkenylcopper compounds [6]. The nature of the products suggests that the thermolysis of Z-$Vi_2Cu_4Br_2$ and Z-$Vi_2Cu_4R_2$ proceeds via release of long-lived propenyl radicals which undergo partial inversion of configuration and are trapped by the solvent rather than by intramolecular Vi—Cu, R—Cu or Br—Cu bonds.

A rather different result was obtained upon thermolysis of the $(Z$-$ViCu_2OTf)_n$ compound (IV) in benzene at 60°C. According to NMR analysis a mixture of isomeric dimers ViVi was isolated in 100% yield. This indicates that the decomposition takes place within the polynuclear $(Z$-$ViCu_2OTf)_n$ cluster. In a recent report the CuOTf-induced synthesis of biaryls via reaction of arylcopper compounds with CuOTf was discussed in terms of electron-transfer processes taking place within a polynuclear precursor complex of the type $Ar_nCu_{n+m}OTf_m$, resulting in the intraaggregate generation of Cu^{II} centres from which biaryls are released via reductive elimination [13] (cf. Scheme 1, path 3). However, the formation of a mixture of isomeric dimers ViVi suggests that the thermolysis of $(Z$-$ViCu_2OTf)_n$ proceeds stepwise and not via path 3 proposed for the CuOTf-induced biaryl synthesis for which full retention of configuration would be expected. For the Vi—Vi coupling path 1 and 2 may be considered. Path 2 involves homolytic cleavage of one C(Vi)—Cu bond with concomitant η^2-bonding of the alkenyl radical to the Cu^0 center formed in the copper cluster. This is followed by intraaggregate trapping of the radical by a neighbouring C(Vi)—Cu bond. This route is essentially similar to the one proposed by Whitesides et al. for the thermal decomposition of cis- and trans-propenylcopper. It is important to note that the latter reaction yields the corresponding hexadienes with retention of configuration [6]. Although the aggre-

SCHEME 1

Possible routes for the thermolysis of the propenylcopper–copper triflate compound Z-$Vi_2Cu_4OTf_2$ (IV)
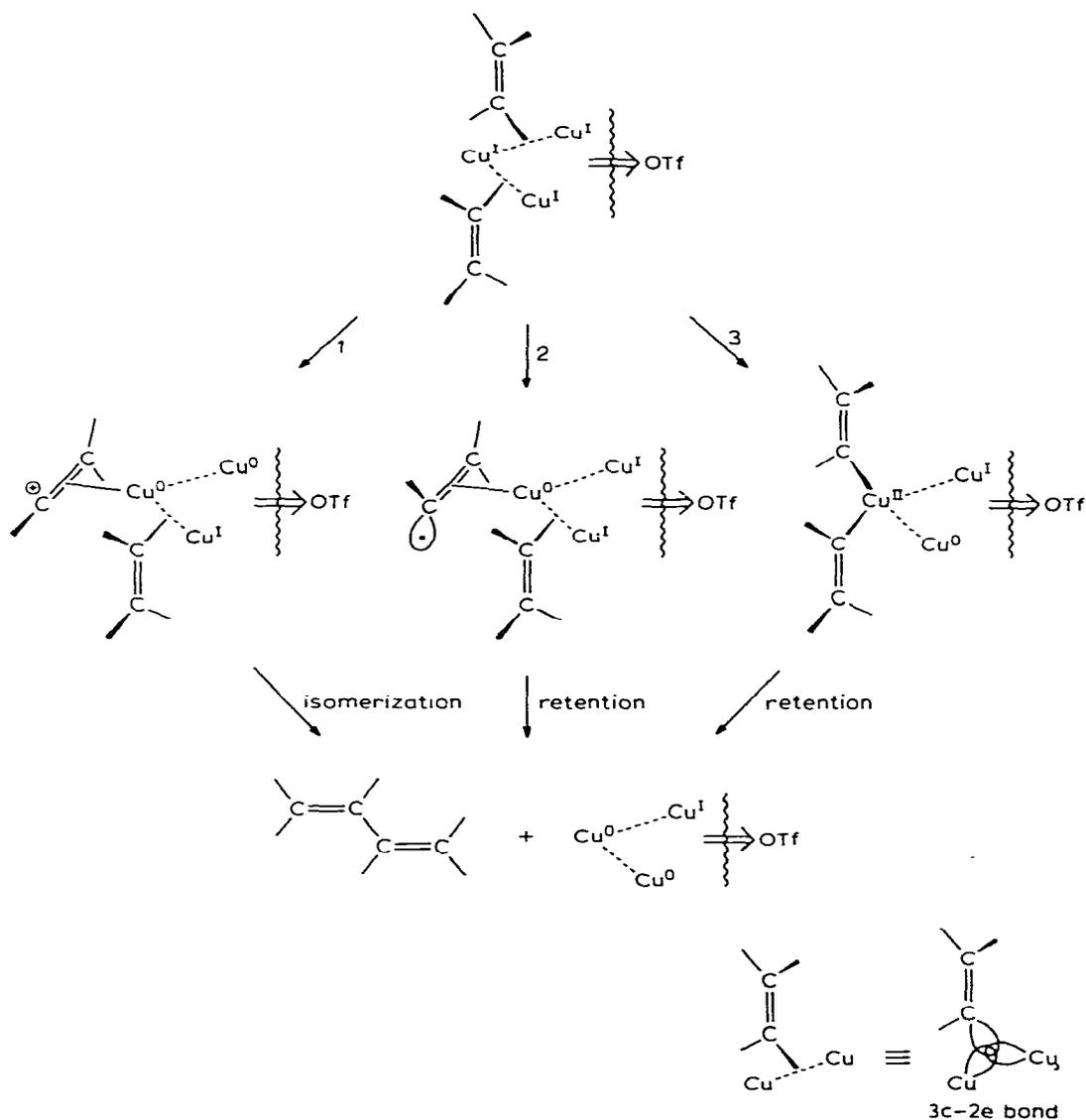
gation state of the latter propenylcopper compounds is unknown, based on our structural work [9] it seems plausible that also these compounds have polynuclear structures.

The observed isomerization in the thermolysis of the mixed propenyl/OTf cluster IV points to path 1 rather than 2 or 3 (Scheme 1). Path 1 involves the formation of an incipient vinyl cation which likewise remains in the coordination sphere of the Cu aggregate by η^2-bonding. This then undergoes C—C coupling via electrophilic attack on a C(Vi)—Cu bond. This process, because of the linearity of the vinyl cation [18], proceeds with retention or inversion of con-

figuration. This proposal seems reasonable in view of the relative stability of vinyl cations and their tendency to undergo isomerization [18].

The quantitative formation of ArAr in the reaction of $Ar_4Cu_6Br_2$ with CuOTf proceeds via ligand displacement followed by an irreversible interaction of $Ar_4Cu_6OTf_2$ with CuOTf [13]. We have observed that a similar mixture of dimers ViVi as obtained in the thermolysis reaction of $(ViCu_2OTf)_n$ results from the addition of an excess of CuOTf to Z-$Vi_2Cu_4Br_2$ (III) and assume that this reaction likewise involves ligand exchange as the first step.

The different results for the thermolysis of Z-$Vi_2Cu_4Br_2$ and $(Z$-$ViCu_2OTf)_n$ is a further illustration of the importance of the influence of the "counter anion" on the reactivity of the copper—carbon bond in organocopper—copper anion cluster compounds.

Chemical behaviour

Hydrolysis reactions

The E-1,2-diarylpropenyllithium compound I and the Z-1,2-diarylpropenyl-copper—copper bromide compound III have been subjected to a series of chemical decomposition reactions. In contrast to the complete retention of configuration observed on hydrolysis of E-ViLi (I) [19], a mixture of isomeric E/Z-1,2-diarylpropenes is obtained on hydrolysis of the copper compound III dissolved in benzene (eq. 3).
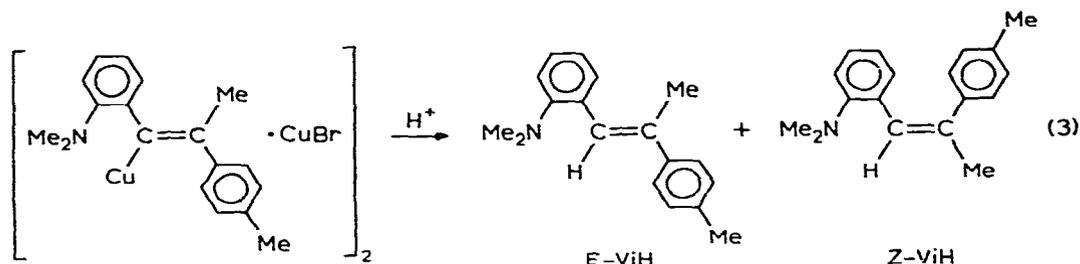
The isomer composition depends on both the hydrolysing agent and the solvent (Table 1).

The observed partial inversion of configuration upon hydrolysis of the Cu—C

TABLE 1

COMPOSITION OF THE MIXTURE OF ISOMERS OBTAINED ON HYDROLYSIS OF Z-$Vi_2Cu_4Br_2$ (III)

Hydrolysing agent	E-ViH	Z-ViH
H_2O	0.70	0.30
MeOH	0.82	0.18
HCl/H_2O (4N)	0.87	0.13
NH_3/H_2O (6 N)	0.88	0.12
HCl gas	0.88	0.12
HOAc	0.91	0.09
HCl/Et_2O	0.93	0.07

bond is unusual and has only been reported for the hydrolysis of configurationally pure alkenylrhodium [20] and -titanium [21] compounds.

In the synthesis of Z-Vi$_2$Cu$_4$Br$_2$ (III) configurationally pure (>98%) E-1,2-diaryl-1-propenyllithium has been used. The Vi$_2$Cu$_4$Br$_2$ compound used in the hydrolysis reaction is likewise configurationally pure (Z-isomer) according to NMR spectroscopy. Contamination with the E-isomer would have been easily detected (see e.g. the different spectra of the isomeric E- and Z-1-propenyltin, E- and Z-1-propenyl halide and E- and Z-1-propene compounds [19]). In separate experiments it was shown that both E- and Z-ViH are configurationally stable in the presence of HCl or a mixture of HCl and a Cu^{II} salt.

The above results indicate that the observed isomerization must take place during the hydrolysis reaction. The latter reaction will most likely proceed via a primary electrophilic attack of H$^+$ on the α-carbon atom perpendicular to the molecular plane of the olefin [20—24]. In the resulting intermediate, in which the double bond is broken and the α-carbon atom has become positively charged (see Scheme 2), rotation around the C$_\alpha$—C$_\beta$ bond has to take place in order to bring the leaving Cu-ion in a position perpendicular to the molecular plane [25] (a and b, Scheme 2).

This rotation can be brought about either by a 60° clockwise rotation (a, Scheme 2), which in the end will give retention of configuration (c) or a 120° counterclockwise rotation (b, Scheme 2) resulting in inversion (d). As the former rotation will proceed more easily than the latter, retention would seem to be the preferred mode of the reaction. However, the final ratio of isolated isomers will be determined by the lifetime of the intermediate species (A, B or C). This lifetime is influenced by the solvent polarity [23,24] as well as by the type of the nucleophilic counterion. Our results show a tendency towards

SCHEME 2

An = 2-Me$_2$NC$_6$H$_4$; Tol = C$_6$H$_4$Me-4. For the hydrolysis reaction X = H; M$_n$ = Cu$_n$. For the halogenation reaction X = Cl, Br; M$_n$ = Cu$_n$ or Ag$_n$.
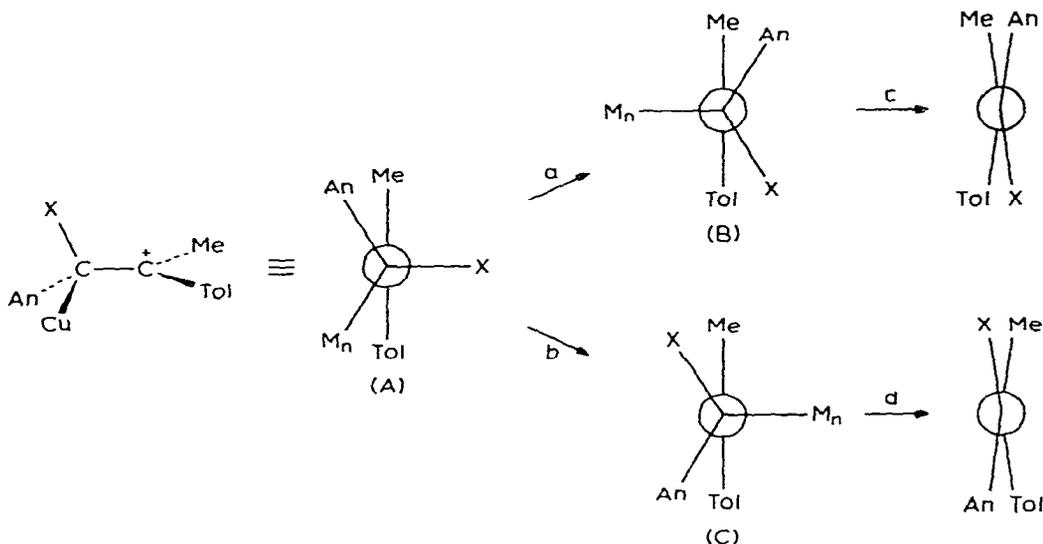
higher selectivity when the reagent used gives rise to a more stable copper/nucleophile complex (NH_3 or OAc^-). The increase in selectivity observed going from HCl/H_2O via HCl_g to HCl/diethyl ether may reflect the actual concentration of the protolysing agent in benzene.

Halogenation reactions

Halogenation reactions of Z-$Vi_2Cu_4Br_2$ (III) with $CuCl_2$ and with I_2 have been investigated. For the interpretation of the results it was necessary to establish the configuration of the propenyl halides which are formed in these reactions.

The formation of alkenyl bromides from the reactions of alkenyllithium compounds with N-bromosuccinimide [26,27] and with 1,2-dibromoethane [6] has been reported to proceed with retention of configuration. We have carried out the halogenation of E-ViLi (I) with the same halogenating agents. Reaction of E-ViLi with N-bromosuccinimide in diethyl ether gave a 1/1 mixture of ViBr and ViH. Based on the assumption that this reaction likewise proceeds with retention of configuration (cf. ref. 26, 27) the ViBr compound formed was assigned the Z-configuration (eq. 4). The NMR spectrum of ViH was identical with that of authentic E-ViH [19] and thus formation of ViH in


Z-ViX (X = Cl, Br or I), E-ViX (X = Cl, Br or I)
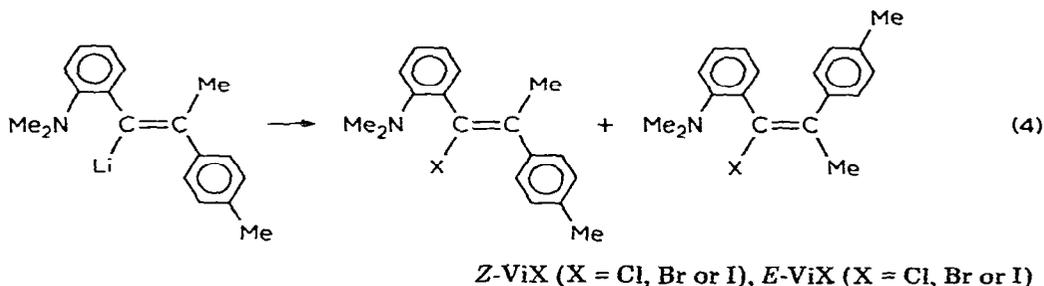
this reaction has proceeded with retention of configuration. Reaction of E-ViLi with 1,2-dibromoethane yielded a mixture of ViBr (61%) and ViH (36%). The respective NMR spectra were identical with those of ViBr and ViH formed in the reaction of E-ViLi with N-bromosuccinimide and are assigned to Z-ViBr and E-ViH, respectively. This assignment is supported by the previously observed retention of configuration in the reaction of alkenyllithium compounds with 1,2-dibromoethane [6]. Reaction of I with I_2 resulted in the formation of a 1/1 mixture of isomeric 1,2-diaryl-1-iodopropenes. The Z-isomer (Z-ViI) was easily identified on the basis of the similarity of its NMR spectrum with that of Z-ViBr. The remaining resonances were assigned to E-ViI (eq. 4).

Based on these results and on the observation that the chemical shift values for the diarylpropenyl halides (ViX) are little dependent on the nature of X (see Table 2) the products formed in the halogenation of Z-$Vi_2Cu_4Br_2$ could now be identified.

Iodination of the Z-$Vi_2Cu_4Br_2$ compound III in benzene gave a mixture of Z-ViI (71%), E-ViI (20%), E-ViH (6.6%) and ViVi (2.4%, mixture of isomers) and thus reaction proceeds predominantly with retention. In a recent report, Normant et al. have shown that the reaction of in situ prepared alkenylcopper compounds with I_2 in diethyl ether at $-20°C$ yields 1-iodo-1-alkenes with com-

TABLE 2

^{1}H NMR SPECTRA DATA ^{a}

Structure	X	Conf.	N(CH$_3$)$_2$	C=CCH$_3$ ^{b}	4-CH$_3$ ^{b}
(ViX)	H	E	2.53	2.18 ^{c}	2.15
	Li	E	2.01	2.18	2.18
	Cl	Z	2.63	1.85	2.13
	Br	Z	2.67	1.85	2.15
	I	Z	2.67	1.90	2.13
	Cu(CuBr)	Z	2.40	2.09	2.23
(ViX)	H	Z	2.63	2.17 ^{c}	2.07
	Cl	E	2.37	2.28	1.95
	Br	E	2.40	2.33	1.95
	I	E	2.42	2.41	1.93
ViVi			2.47/2.52 ^{d}	1.70 ^{d} (?)	2.27/2.24 ^{d} (?)
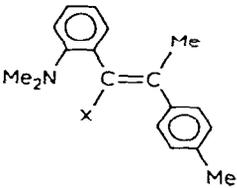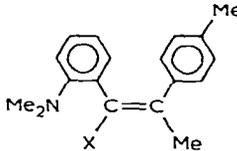
^{a} δ(H) [C$_6$D$_6$, TMS internal, δ(ppm)]. ^{b} Assignment based on the observed line width difference. ^{c} For ViH: ^3J(H—C) trans $> ^3J$(H—C) cis, see ref. 19. ^{d} Nonseparable mixture of isomers.

plete retention of configuration in giving the 1-iodo-1-alkenes [28].

Addition of CuCl$_2$ to a benzene solution of III yields a mixture of E-ViX (63%) and Z-ViX (37%). According to mass spectrometry ViX is a mixture of ViBr and ViCl in about 3/1 molar ratio. The reaction of E-ViLi (I) with CuCl$_2$ in diethyl ether, which was studied for comparison, yielded ViVi (mixture of isomers), E-ViCl and Z-ViCl in about 50, 30 and 20% yield, respectively. In both reactions of CuCl$_2$ the formation of ViX proceeds with inversion of configuration rather than with retention (amount of E-ViX > amount of Z-ViX). The formation of ViVi in high yield in the reaction of E-ViLi (I) with CuCl$_2$ contrasts with the absence of ViVi in the corresponding reaction of Z-Vi$_2$Cu$_4$-Br$_2$ (III).

The yields of the various reaction products mentioned above have been determined by NMR spectroscopy of the reaction mixtures. NMR data of the various compounds are given in Table 2.

In recent years the nature of the interaction of organolithium (RLi) and organocopper (RCu) compounds with copper(II) halides (CuX$_2$) has received attention [14,29]. Such reactions generally result in the formation of RR, RX and RH in various ratios [3]. The formation of these products has been explained on the basis of an intramolecular electron-transfer redox reaction taking place in innersphere activated complexes of the type $[R_nM_{n-1}^IM^I\cdots X\cdots Cu^{II}X(Cu^{II}X_2)_{m-1}]$ to give $[R^{\cdot}R_{n-1}M_{n-1}^IM^IX\cdots Cu^IX(Cu^{II}X_2)_{m-1}]$ [29]. Release of free radicals R$^{\cdot}$ accounts for the presence of RH, which is formed in small amounts only. Formation of RR and RX is explained by a concerted

side on view   end on view
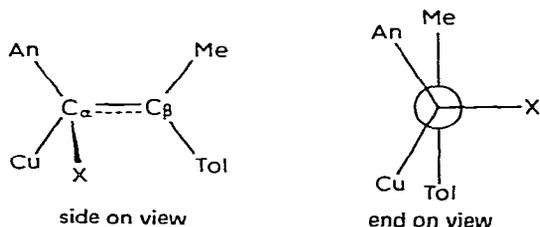
Fig. 2.

intramolecular process (attack of R$^{\bullet}$ on a M^{I}—R or a Cu^{II}—X bond).

Formation of ViH is not observed in the reaction of both E-ViLi and Z-Vi$_2$-Cu$_4$Br$_2$ with CuCl$_2$ which would seem to rule out a mechanism involving free radicals. The formation of ViX proceeds to a large extent with inversion of configuration (E-ViX > Z-ViX). Moreover, for the ViX compounds obtained from the reaction of Z-Vi$_2$Cu$_4$Br$_2$ with CuCl$_2$ a ViBr/ViCl ratio of 3/1 was established *. These observations suggest that these reactions proceed partly or even completely via a concerted mechanism.

The first step of a concerted mechanism for the reaction of Vi$_2$Cu$_4$Br$_2$ with CuCl$_2$ may involve formation of an innersphere activated complex of the type [Vi$_2$Br$_2$Cu$_3^I$Cu$^I\cdots$Cl$\cdots$Cu^{II}Cl(Cu^{II}Cl$_2$)$_{n-1}$] (cf. ref. 29). A species [Vi$_2$Br$_2$-Cu$_3^I$Cu^{II}Cl$\cdots$Cu^{I}Cl(Cu^{II}Cl$_2$)$_{n-1}$] is generated via intramolecular electron-transfer which is then followed by reductive elimination of ViX (X = Cl or Br) **

In the reductive elimination intraaggregate attack of halide on C(α) (Fig. 2) is assumed to proceed almost perpendicular to the molecular plane of the propenylcopper compound, probably via a three-centre transition state [25,33] (see Fig. 2), resulting in the formation of an intermediate in which C(α) has become sp^3-hybridized and in which the double bond has been broken, leaving C(β) in the planar configuration [25]. Rotation around $C(\alpha)$—$C(\beta)$ is required to bring the leaving group in a position perpendicular to the plane of the resulting propenyl halide (cf. Scheme 2 on page 333).

The elimination of the leaving group in nucleophilic substitution reactions is generally observed to be very fast and retention of configuration, resulting from primary rotation over the smallest angle (route a + c, Scheme 2) is found [33]. In a few cases, however, inverted products have been isolated [34]. Similarly, we observe that partial inversion of configuration occurs. These results can be interpreted in terms of enhanced lifetimes for the intermediate species (A, B or C, Scheme 2). Electronic *trans* effects (X *trans* to Tol instead of Me) will play an important role in the determination of the final configuration [25].

Upon reductive elimination of ViX from the encounter complex [Vi$_2$Br$_2$-Cu$_3^I$Cu^{II}Cl$\cdots$Cu^{I}Cl(Cu^{II}Cl$_2$)$_{n-1}$], formally a Cu^0 atom is generated. Because Cu^0

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* Bromine/chlorine exchange of ViBr with CuCl$_2$ is very unlikely to proceed under the conditions used [14].

** The CuOTf-induced selective biaryl synthesis from arylcopper compounds similarly involves reductive elimination from Cu^{II} centres [13]. Reductive elimination processes from oxidized centres may also account for the C—C coupling which takes place on addition of nitrobenzene to lithiumcuprates [30] and in the reaction of lithiumcuprates with alkyl halides [31] (Corey-Posner reaction [32]).

has never been observed as a reaction product, it is assumed that electron transfer from Cu^0 to Cu^{II} takes place in the encounter complex immediately after elimination of ViX (cf. ref. 14). The electron transfer processes which have to occur during the reductive elimination may account for the increased lifetime of the intermediate species (A, B or C, Scheme 2).

Reaction of E-ViLi (I) * with $CuCl_2$ similarly may proceed via an encounter complex of the type $[Vi_nLi_n\cdots Cl\cdots Cu^{II}Cl(Cu^{II}Cl_2)_{m-1}]$. Intramolecular electron-transfer reduction of Cu^{II} will result in the formation of a species $[Vi^\bullet Vi_{n-1}Li_nCl\cdots Cu^ICl(Cu^{II}Cl_2)_{m-1}]$. The Vi radical may attack either a Li—C bond with formation of ViVi or a Cl—Cl bond with formation of ViCl. The latter reaction may proceed via a transition state similar to that depicted in Fig. 2 for the reaction of $Vi_2Cu_4Br_2$.

With respect to the C—C coupling process, the quantitative intramolecular C—C coupling taking place in the reaction of $Mg[C_6H_4CH_2N(Me)CH_2CH_2N(Me)-CH_2C_6H_4]$ with $CuCl_2$ (eq. 5) is worth noting [35].

$$+ \ 2 \ Cu^ICl\cdot(Cu^{II}Cl_2)_n\cdot MgCl_2 \tag{5}$$
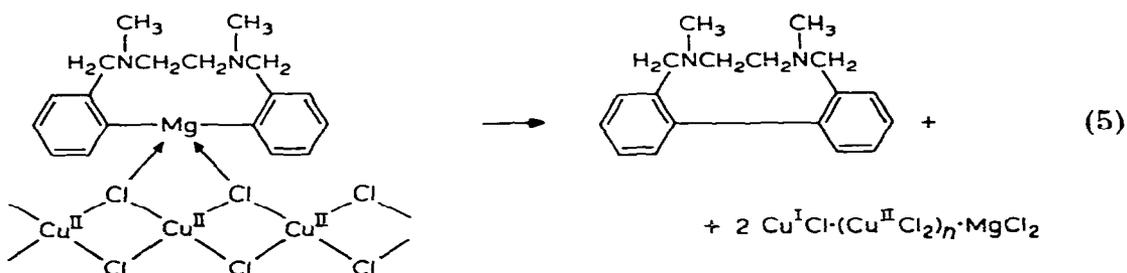
Attempts to synthesize $(Z\text{-ViAgBr})_n$, the silver analog of III, via reaction of E-ViLi (I) with silver bromide were unsuccessful. Interestingly, the latter reaction yielded E-ViH (IX, 23% yield) and the inverted 1,2-diaryl-1-propenyl-bromide E-ViBr (X, 67% yield), eq. 6:

$$\tag{6}$$
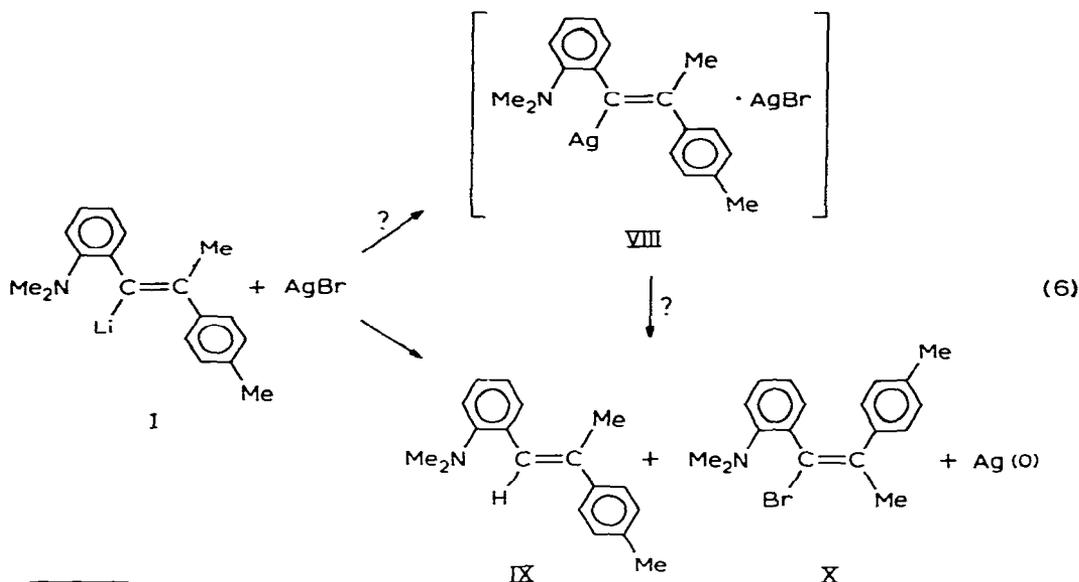
* This compound exists as a dinuclear species E-Vi_2Li_2 in benzene [19].

The formation of E-ViBr may proceed via the intermediate formation of $(Z\text{-ViAg}_2\text{Br})_n$ (VIII) (eq. 6). In view of the easily occurring light-induced formation of Br radicals from AgBr, intraaggregate attack of Br radicals on the Ag—C bond, again via a transition state of the type shown in Fig. 2, would seem likely.

The partial inversion of configuration (isolation of a mixture of E- and Z-isomers) upon reaction of E- or Z-1-propenyl- and E- or Z-1-butenylmercury bromide compounds with I_2 in non-polar degassed solvents has been interpreted in terms of a radical-type reaction [36]. Reaction of E-ViLi (I) with I_2 produces a 1/1 mixture of E-ViI and Z-ViI suggesting that this reaction is likewise radical in nature. The observation that the reaction of Z-Vi$_2$Cu$_4$Br$_2$ with I_2 proceeds with predominant retention of configuration (Z-ViI, 73%; E-ViI, 20%) might indicate that this reaction at least in part involves electrophilic attack of I^+ on $C(\alpha)$ (cf. Scheme 2).

Experimental

General

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried and distilled in a nitrogen atmosphere before use.

The following compounds have been prepared according to published methods: cupric chloride [37], cuprous triflate [38], E-1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium (I) [19] and the 1,2-diarylpropenylcopper compounds III—VII [7].

Mass spectra were obtained from a Finnigan 3100 D Gaschromatography/Mass Spectrometer by Mrs. G.G. Versluis-de Haan and Mrs. C.M. Bijlsma-Kreuger. ^{1}H NMR spectra were recorded on a Varian Associates T-60 spectrometer.

Thermolysis

Z-bis[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]-tetrakiscopper dibromide (III). A mixture of III (400 mg) and naphthalene (10 g) was heated for 8 min at 220°C. A copper mirror was formed. After removal of the naphthalene by sublimation at 100°C, benzene was added. Only Z-ViH (27%) and E-ViH (63%) were formed according to NMR analysis. For NMR data see Table 2.

Z-[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]bis-copper trifluoromethanesulphonate (IV). A suspension of IV (200 mg) in benzene (20 ml) was warmed at 60°C for 30 min. After cooling, ammonia (6 N) was added. The benzene layer was separated, washed with water, dried over MgSO$_4$ and evaporated. A white solid residue was isolated. According to NMR spectroscopy this white solid was a mixture of dimers (ViVi). For NMR data see Table 2. Mass spectral data (solid probe, m/e): 500 (M^+), 485, 409, 381, 119, 104, 91 (high intensity fragment ions): calcd. for $C_{36}H_{40}N_2$ (ViVi): 500.

Z-[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl]-1-propenyl]-(4-methylphenylethynyl)biscopper (VI). A solution of 4-methylphenylacetylene (2.58 mmol) in diethyl ether (15 ml) was added to n-butyllithium in hexane (1.4 ml, 1.7 N, 2.38 mmol). The obtained suspension was stirred for 45

min and then added to a suspension of III (2.4 mmol) in benzene (75 ml). The colour of the mixture changed from yellow to dark-brown. After 2 h the clear solution was evaporated. A very dark oil remained. After addition of benzene (30 ml) the obtained suspension was centrifuged (2000 c/s, 20 min). The greenish-brown supernatant was decanted and evaporated, leaving an oily residue. This oily residue was mixed with naphthalene (11 g) and the mixture heated for 3 h at 150°C. After cooling to room temperature, benzene was added. An NMR spectrum of the resulting solution revealed the presence of E-ViH and Z-ViH. For NMR data see Table 2. By solid probe mass spectroscopy a small amount of asymmetric coupling product (ViR, ~5%) could be detected. Mass spectral data (m/e: 365/364 ($M^+/M^+ - 1$), 350/349 (high intensity fragment ions); calcd. for $C_{27}H_{27}N$ (ViR): 365.

Z-bis[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]bis-(2-N,N-dimethylaminophenyl)tetrakiscopper (VII). A suspension of VII (250 mg) in decaline (20 ml) was heated for 20 min at about 190°C. A copper mirror was formed. After cooling, the solution was extracted with hydrochloric acid (4 N). The extract was neutralized with ammonia (6 N) and extracted with diethyl ether. The ether solution was washed with water, dried over $MgSO_4$ and evaporated. The NMR spectrum showed coinciding resonance lines of the compounds Z-ViH, E-ViH, RH and ViR. Tentatively assigned NMR data for the asymmetric coupling product ViR (C_6D_6, TMS internal, δ(ppm): 2.53 (NMe_2), 2.16 (4-Me and C=CMe)). GLC showed a 20% yield of ViR. Mass spectral data for ViR (m/e): 370 (M^+), 251, 236, 119, 91 (high intensity fragment ions); calcd. for $C_{26}H_{30}N_2$ (ViR): 370.

Reaction of Z-Vi$_2$Cu$_4$Br$_2$ (III) with CuOTf

Excess of cuprous triflate was added to a suspension of III (0.7 mmol) in benzene (20 ml). The colour of the suspension changed from green to red-brown. After 20 h ammonia was added and the mixture was extracted with diethyl ether. The ether extract was washed with water, dried over $MgSO_4$ and evaporated, leaving a mixture of isomeric dimers (ViVi, 92%) and E-1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propene (E-ViH, 8%). For NMR data see Table 2.

Chemical decomposition reactions

Reaction of E-1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium (I).

With H_2O: see ref. 19.

With iodine: A solution of iodine (4 mmol) in diethyl ether (20 ml) was added to a solution of I (3.33 mmol) in diethyl ether (35 ml). After stirring for $\frac{1}{2}$ h, the ether solution was washed with water, dried over $MgSO_4$ and evaporated, giving a 1/1 mixture of the Z- and E-ViI compounds in quantitative yield, according to NMR spectroscopy. For NMR data see Table 2. Solid probe mass spectral data (m/e): 377 (M^+), 250, 119 (high intensity fragment ions); calcd. for $C_{18}H_{20}NI$ (ViI): 377. Identical results are obtained on addition of solid I_2 to a benzene solution of I.

With N-bromosuccinimide: A solution of I (4 mmol) in diethyl ether (40 ml) was added to a suspension of an excess of NBS (5 mmol) in the same solvent

(20 ml). The mixture was stirred for 2 h. On addition of water the white precipitate which had formed dissolved. The ether solution was separated and worked up as described above. An oil was isolated containing Z-ViBr (50%) and E-ViH (50%) according to NMR spectroscopy.

With 1,2-dibromoethane: A solution of I (6.7 mmol) in diethyl ether (60 ml) was added to an excess of 1,2-dibromoethane (20 ml) (predried on Na_2SO_4, filtrated over Al_2O_3) [6]. The solution was washed with water, dried over $MgSO_4$ and evaporated. The residual oil consisted of Z-ViBr (64%) and E-ViH (36%) according to NMR spectroscopy.

With cupric chloride: A solution of I (5 mmol) in diethyl ether (40 ml) was added to an equimolar amount of $CuCl_2$ (5 mmol) suspended in diethyl ether (20 ml). After 15 min the ether solution was decanted from a white precipitate, treated with ammonia, washed with water, dried over $MgSO_4$ and evaporated. According to NMR spectroscopy the residual oil consisted of ViVi (mixture of isomers, about 50%), E-ViCl (about 30%) and Z-ViCl (about 20%).

Reaction of Z-$Vi_2Cu_4Br_2$ (III) with hydrolysing agents. A standard solution of III (0.7 mmol) in benzene (140 ml) was prepared. 1,4-ditert-butylbenzene (1 mmol) was used as an internal reference for NMR analysis. To aliquots (20 ml) of this solution were added: water (20 ml; slow decomposition), methanol (20 ml; slow decomposition), HCl/H_2O (4 N) (20 ml; rapid decomposition), ammonia (6 N) (20 ml; slow decomposition), glacial acetic acid (10 ml; rapid decomposition, formation of a white precipitate) and HCl in diethyl ether (6 ml of saturated solution; rapid decomposition). In a further experiment gaseous HCl was passed through the solution (20 ml). A general work-up procedure was used. After reaction the solution was neutralized by addition of ammonia (6 N). The organic products were isolated by extraction with diethyl ether. The ether extract was washed with water, dried over $MgSO_4$ and evaporated. The obtained residue was analysed by NMR spectroscopy. According to the internal standard quantitative conversion had taken place. The ratio of the isomeric diaryl propenes formed has been summarized in Table 1.

Reaction of Z-$Vi_2Cu_4Br_2$ (III) with I_2. A solution of iodine (0.3 mmol) in benzene (10 ml) was added to a benzene (10 ml) solution of III (0.25 mmol). Addition of iodine was stopped at the moment when iodine was no longer consumed as indicated by the violet colour of the resulting suspension. According to NMR analysis the solution contained Z-ViI (71%), E-ViI (20%), E-ViH 6.6%) and ViVi (2.4%).

Reaction of Z-$Vi_2Cu_4Br_2$ (III) with $CuCl_2$. An excess of $Cu^{II}Cl_2$ (2 mmol) was added to a solution of III (0.1 mmol) in benzene (20 ml), resulting in the formation of a colourless suspension. After treatment with ammonia (6 N) the mixture was extracted with diethyl ether. The extract was washed with water, dried over $MgSO_4$ and evaporated. According to NMR analysis a quantitative reaction had taken place (1,4-ditert-butylbenzene, internal reference), giving E-ViX (X = Cl, Br) (63%) and Z-ViX (37%). Solid probe mass spectroscopy gave an estimated Br/Cl ratio of 3/1. Mass spectral data (m/e): 331 (intensity 3904), 329 (intensity 4160), 287 (intensity 704), 285 (intensity 2176). Calcd. for $C_{18}H_{20}NX$: 331 (^{81}Br), 329 (^{79}Br), 287 (^{37}Cl), 285 (^{35}Cl).

Reaction of E-ViLi (I) with AgBr

A solution of I (3.33 mmol) in diethyl ether (35 ml) was added in 15 min to a suspension of AgBr (6.92 mmol) in diethyl ether (20 ml) at —25°C without exclusion of light. A dark-green to black precipitate was formed. After 2 h the temperature was raised to room temperature. The supernatant liquid was decanted from metallic-brown pellets. These pellets were insoluble in benzene and did not change when exposed to air. The liquid was treated with water, dried over MgSO$_4$ and evaporated, yielding 0.65 g of an oil, which according to NMR analysis was a mixture of Z-ViH (8%), E-ViH (25%) and E-ViBr (67%). For NMR spectral data see Table 2.

Acknowledgement

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