

REACTIONS OF THE AROMATIC ORGANOCOPPER COMPOUNDS WITH CHOSEN BORON COMPOUNDS

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Summary

The reaction of arylorganocopper compounds Cu_4Ar_4 ($\text{Ar} = \text{Ph}$, $\text{C}_6\text{H}_4\text{CH}_2\text{-NMe}_2$ -2) with BR_3 boron compounds (BF_3 , BEt_3 , BPh-9-BBN , BAr-9-BBN , $\text{Ar} = \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ -2-9-BBN = 9-borabicyclo[3.3.1]bicyclononyl) was investigated. A mechanism involving polymer formation in the first step of the reaction with subsequent intramolecular rearrangement under abstraction of $\text{BR}'\text{R}_2$ is proposed.

Introduction

Bimetallic compounds containing copper and a Main Group element (e.g. Li, Mg) are well known in the field of organic synthesis. The strong tendency of organocopper compounds to form complexes of various stoichiometry with other organometallics is very advantageous with regard to their catalytic properties [1–3]. The application of the cuprates $\text{RCu} \cdot \text{M}^n\text{R}_n$ (M is a Main Group metal e.g.: Li, Mg, B, Al, Sn) permitted us to carry out many stereoselective and stereospecific reactions.

In the late seventies organocopper complexes with BF_3 and BR_3 were shown to be excellent catalysts for substitution reactions of alkyl halides [4], conjugated addition to α,β -unsaturated carbonyl compounds [5], and stereospecific substitution of a methyl group [6]. In the reaction with an allyl alcohol they give mainly an alkene with allylic rearrangement [7].

Unfortunately the same properties of organocopper compounds are responsible for the formation of bimetallic catalysts and for the difficulties in separating the organocopper compounds from their bimetallic derivatives. Moreover it should be mentioned that the Cu–C bond is very oxidatively, hydrolytically and in most cases thermally unstable. Despite these facts it has been reported during the last decade that several organocopper and polynuclear bimetallic compounds [8] were isolated. In many cases their structures in the solid state and in solution were characterized.

Cluster species with four [9] and six [10] metal atoms were described. The

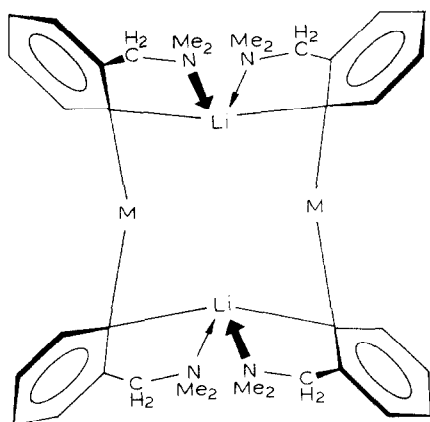


Fig. 1. Proposed structure of tetranuclear $(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_4\text{Cu}_2\text{Li}_2$ [9b].

structure of the organocopper compounds strongly depends on the ligands bonded to the metal atoms. It was shown that both organocopper and bimetallic organocopper compounds containing an aromatic ligand can exist as cluster species with the metal atoms bonded via 3 center-2 electron (3c-2e) carbon bridges (Fig. 1, 2).

It is noteworthy that for insoluble organocopper compounds the polymeric structure has been proposed. Analogically to the cluster structures, solved by means of X-ray spectroscopy, the 3c-2e bonds are proposed for polymeric $(\text{PhCu})_n$ complexes [11] (Fig. 3).

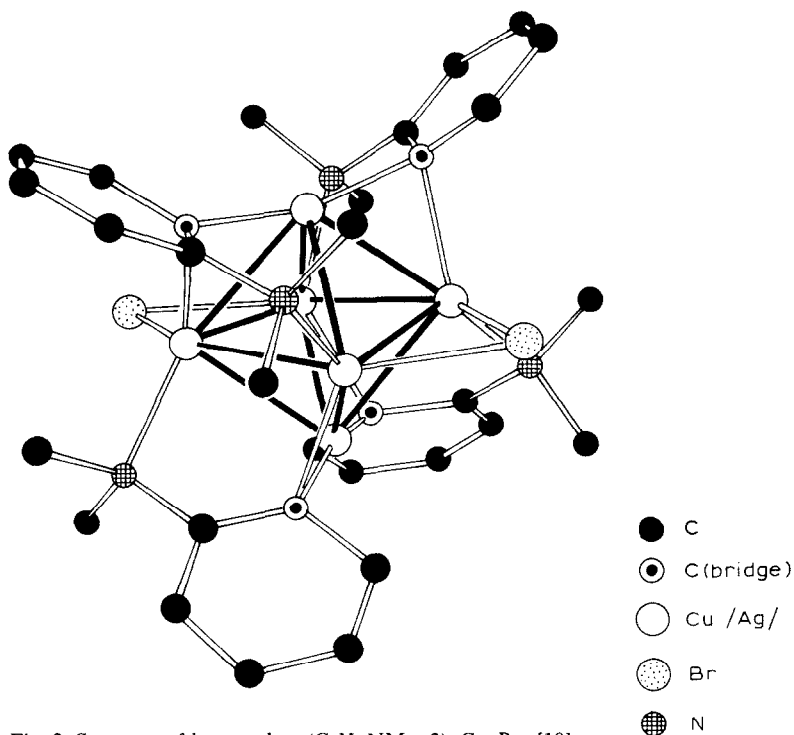


Fig. 2. Structure of hexanuclear $(\text{C}_6\text{H}_4\text{NMe}_2\text{-}2)_4\text{Cu}_6\text{Br}_2$ [10].

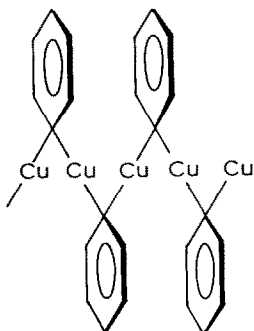


Fig. 3. Proposed structure of polymeric $(\text{CuPh})_n$.

Until now there are no reports in the literature on reactions of organocopper compounds with organoboranes and on the physico-chemical properties of organo-copper-boron compounds. It was only reported that polymeric CuBPh_4 [12] was obtained by direct synthesis from PhCu and BPh_3 .

The synthesis and investigation of the physico-chemical properties of the organoboron-copper compounds chosen were the main aims of this research. The CuPh and Cu_4Ar_4 ($\text{Ar} = \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ -2) compounds were chosen since they belong to the most stable organocopper compounds. The compounds used as substrates or models, containing at least one aromatic ring bonded to boron (e.g. BPh-9-BBN , BAr-9-BBN , $(\text{BAr-Ph-9-BBN})\text{Li} \cdot \text{OEt}_2$, $\text{Ar} = \text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ -2, 9-BBN = 9-borabicyclo[3.3.1]nonyl) were previously synthesized and characterized [13]. We expected that the organocopper-boron species with the $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ -2 ligand and with a bulky 9-BBN ring which sterically inhibit decomposition pathways should be sufficiently stable for physico-chemical research. Moreover, more simple but less stable systems with BF_3 and BEt_3 were also investigated.

Results and discussion

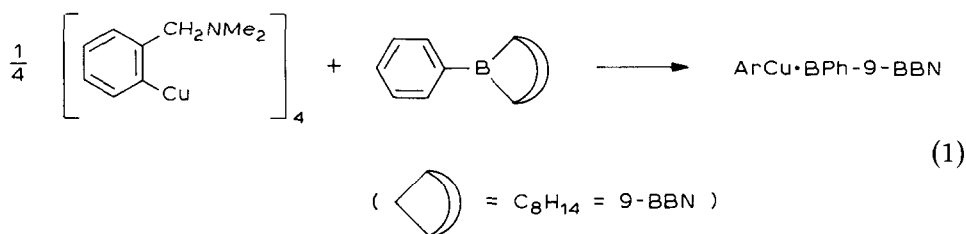
The reactions of CuPh with BF_3 , BEt_3 and of Cu_4Ar_4 with BEt_3 , BPh-9-BBN and BAr-9-BBN were performed in polar solvents at various temperatures. The reaction conditions and product characteristics are listed in Table 1. The reactivity of the boron compounds toward Cu_4Ar_4 increases in the following order: $\text{BAr-9-BBN} < \text{BPh-9-BBN} < \text{BEt}_3 < \text{BF}_3$.

The reaction of CuPh with BF_3 leads, even at low temperatures (Exp. 1), to formation of a black solid containing Cu^0 . In the separated reaction products of CuPh with BEt_3 (Exp. 2, 4) Cu^0 was also present. In the case of the reaction of CuPh and Cu_4Ar_4 with BEt_3 (Exp. 5–8) three fractions of products were separated and identified as: (1) unreacted organocopper substrate, (2) solids containing both copper and boron at various molar ratios (Exp. 4, 6–8) and (3) Cu^0 as decomposition product. It seems that the reaction and decomposition reaction temperatures are very close to each other. The reaction of Cu_4Ar_4 with BPh-9-BBN proceeds without side reactions and it was possible to separate yellow solids (Exp. 9) containing copper and boron. The presence of strong donor solvent e.g. THF favours the decomposition reaction with the formation of Cu^0 .

TABLE 1. REACTIONS OF CuAr WITH BR₃; SUBSTRATES, REACTION CONDITIONS AND PRODUCT CHARACTERISTICS

No.	Substrates	Ratio		Solvent	Temperature (K)	Time (h)	Products	Analysis (found(calcd.)(%))			Stoichiometry ^a of the products
								Cu	B	Cu/B	
1	CuPh + BF ₃	2/1		Et ₂ O	203	2	black solid	50.11 (52.9)	2.34 (2.25)	4/1	[Cu ₂ ⁰ (PhCu) ₂ BF ₃] ^b
2	CuPh + BEt ₃	1/6		Et ₂ O/hexane	263	4	grey solid	43.1 (45.2)	—	—	CuPh
3	CuPh + BEt ₃	1/1.5		Et ₂ O/hexane	263	12	grey solid	55.58 (55.29)	—	—	[Cu ⁰ (CuPh) ₂] ^b
4	CuPh + BEt ₃	1/6		Et ₂ O	203–273	1	green solid	26.8 (27.68)	3.34 (3.14)	3/2	[Cu ⁰ (CuPh) ₂ (BEt ₃) ₂ ·(OEt ₂) ₂] ^{b,c}
5	CuAr + BEt ₃	1/1		Et ₂ O/hexane	253	12	yellow solid	32.52 (32.15)	—	—	CuAr
							green solid	38.31 (41.4)	0.41		[$\frac{1}{2}$ Cu ⁰ CuAr, B traces] ^b
6	CuAr + BEt ₃	1/1		Et ₂ O/hexane	r.t.	12	yellow solid	29.76 (29.7)	0.86 (0.84)	6/1	[(CuAr) ₆ BEt ₃]
7	CuAr + BEt ₃	1/3		Et ₂ O/hexane	253	36	black solid yellow solid	33.36 (32.15)	—	—	Cu ⁰ CuAr
							green solid	18.9 (18.4)	2.11 (3.13)	3/2	[(CuAr) ₃ (BEt ₃) ₂]
8	CuAr + BEt ₃	1/6		Et ₂ O/hexane	r.t.	2	black solid grey solid	50.68 (43.5)	4.3 (3.7)	2/1	Cu ⁰ [Cu ₃ ArCu(BEt ₃) ₂] ^b
9	CuAr + BPh-9-BBN	1/1.4		Et ₂ O	273	3	yellow solid (a) yellow solid (b)	20.19 (19.28)	3.28 (2.04)	3/2	[(CuAr) ₃ (BPh-9-BBN) ₂]
							decomposition products	18.57 (16.10)	3.88 (2.73)	1/1	CuAr-BPh-9-BBN
10	CuAr + BPh-9-BBN	1/1		THF	273						
11	CuAr + BAr-9-BBN	1/1		Et ₂ O	b.p.	70	no reaction				
12	CuAr + BAr-9-BBN	1/1		THF	b.p.	70					

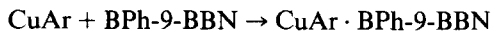
^a The stoichiometry proposed in square brackets is mainly based on the copper and boron contents. ^b In the case when Cu⁰ and CuPh or CuAr are both present in the same brackets it was impossible to wash out Cu⁰ from the organocopper part. ^c The presence of Et₂O was shown in the ¹H NMR spectra.



SCHEME 1

Reaction of Cu₄(C₆H₄CH₂NMe₂-2)₄ with BPh-9-BBN

To a solution of BPh-9-BBN in diethyl ether a solution of Cu₄Ar₄ in diethyl ether was added dropwise at room temperature. The decomposition reaction does not proceed under these conditions. Two fractions of the yellow solid (Exp. 9, fractions (a) and (b)) were isolated. Only fraction (b) has a stoichiometry in accord with reaction Scheme 1. Fraction (a) contains copper and boron at Cu/B 3/2 ratio. The IR (Fig. 4) and ¹H NMR (Table 2) spectra of solid (a) are very similar to those of solid (b). These solids are less soluble in common organic solvents than Cu₄Ar₄ itself. In further investigations our attention was focussed on the reaction:



The reaction 1 in C₆H₆ proceeds slowly at room temperature. The ¹H NMR spectra show that only 50% of the starting amount of Cu₄Ar₄ reacted during one hour. The reaction was completed after 5 h. Finally only one pattern of the signals at 3.20 and 2.03 ppm was observed for the NCH₂ and NCH₃ protons, respectively.

The stability of the Cu-C bond in the CuAr · BPh-9-BBN complex is decreased in comparison with that of the Cu-C bond in Cu₄Ar₄ itself. Cu₄Ar₄ decomposes in the solid state at about 451 K and the CuAr · BPh-9-BBN complex decomposes already at 353 K giving the products shown in Scheme 2.

The formation of Cu⁰ and Ar-Ar in the coupling reaction is common for various organocopper compounds. The presence of BAr-9-BBN results from an exchange

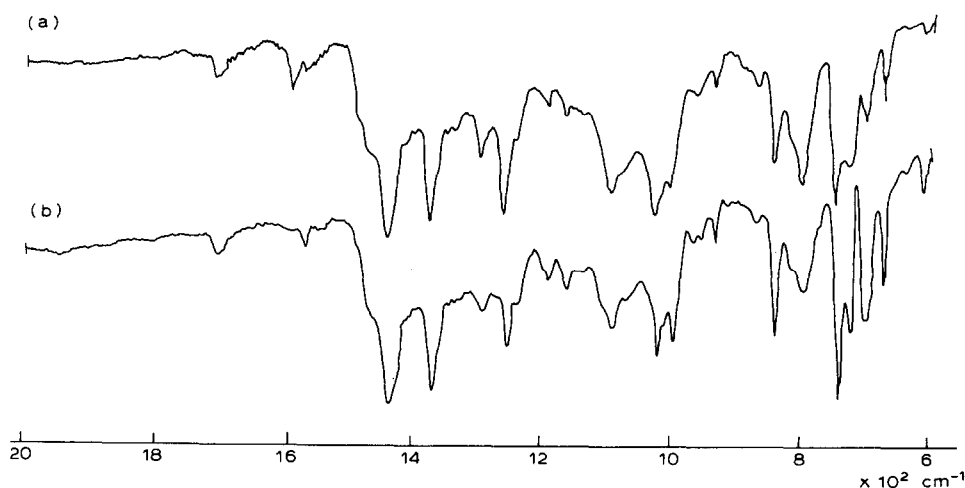
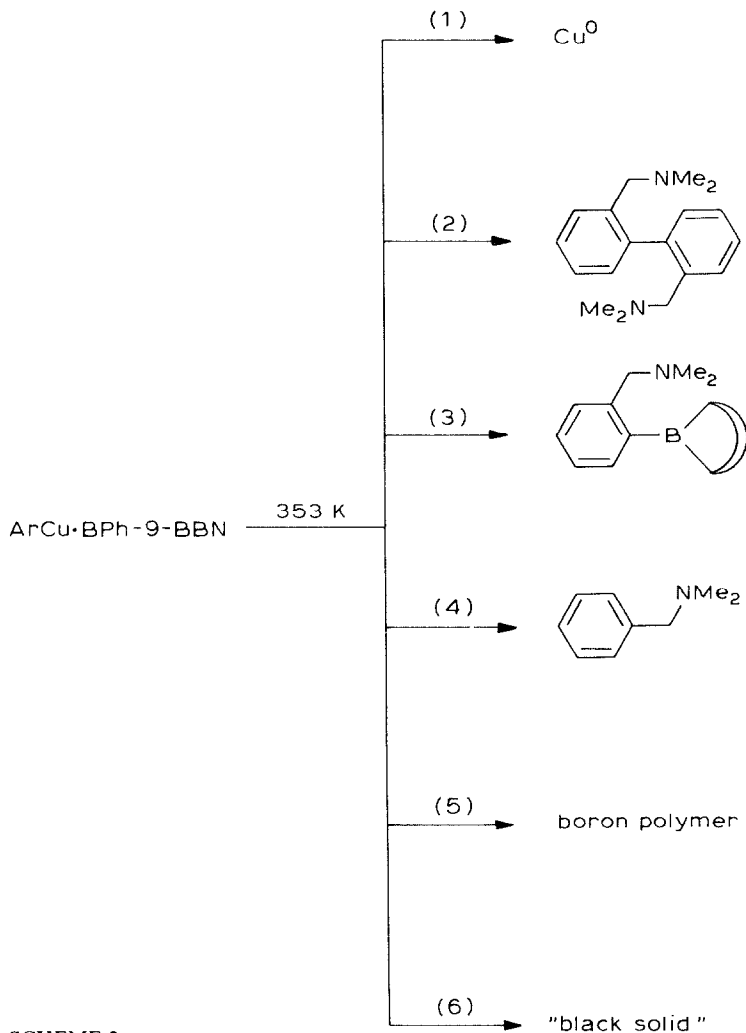


Fig. 4. IR spectra of - yellow solid fraction (a), and yellow solid-fraction (b).



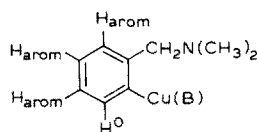
SCHEME 2

reaction. The ArH product (no. 4) was detected among the decomposition products but its origin is not clear.

Fraction no. 5 in Scheme 2 remained unidentified. This was an oily substance with a boron content of 6.3% which can be assigned to a boron polymer.

The fraction described as "black solid" had a Cu^0 content of 48.77% and contained the remaining organic residue. This solid product is completely insoluble in common organic solvents including pyridine. We cannot distinguish if this is either $\text{Cu}_m^0\text{Cu}_n^1\text{Ar}_x\text{Ph}_y$ or $\text{Cu}_p^0(\text{Ar-Ar})_q(\text{Ph-Ph})_r(\text{Ar-Ph})_s$. The black solid does not contain boron and Ph-Ph, Ar-Ph and CuPh were not detected, but their formation cannot be excluded. On the basis of analysis of the decomposition products and ^1H NMR measurements we drew conclusions on the structure of $\text{ArCu} \cdot \text{BPh-9-BBN}$. The ^1H NMR chemical shifts show that an aryl ligand in this complex is not bonded to copper nor to boron exclusively. Moreover, the presence of BAr-9-BBN among the decomposition products let us presume that an aryl ligand should be bonded to

TABLE 2

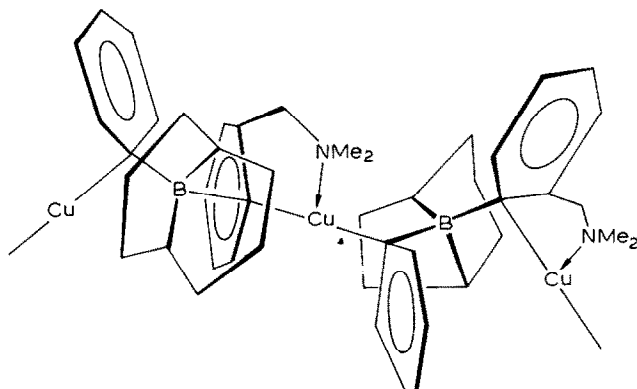
¹H NMR DATA OF CuAr·BPh-9-BBN AND (CuAr)₃(BPh-9-BBN)₂

Compound	Solvent ^b	δ(ppm) ^a				
		H ^o ^c	H _{arom}	NCH ₂	NCH ₃	C ₈ H ₁₄ ^d
CuAr·BPh-9-BBN	CDCl ₃	8.40	7.38	3.53	2.30	1.83
	C ₆ D ₆	8.54	7.20	3.20	2.03	1.82
(CuAr) ₃ (BPh-9-BBN) ₂	CDCl ₃	8.12	7.28	3.44	2.20	1.81
	C ₆ D ₆	8.39	7.11	3.11	1.09	
B-Ar-9-BBN	CDCl ₃	7.78	7.16	3.97	2.45	1.9
	tol- <i>d</i> ₈	8.00	7.25	3.38	2.10	1.8
[B-Ar-Ph-9-BBN]Li·OEt ₂	CDCl ₃	7.61	7.27	3.88	2.66	1.92
	tol- <i>d</i> ₈	8.38;	7.15	3.80	1.95	2.10
		7.93				

^a δ relative to internal TMS. ^b Spectra were recorded for saturated solutions, nevertheless at very low concentrations. ^c H^o = *ortho* protons of the Ar or Ph ring with respect to the C–B or C–Cu bond. ^d The protons from C₈H₁₄ appear as a broad multiplet at a maximum as shown in Table 2.

both copper and boron. An aryl ligand bonded to two different metal atoms via a 3c–2e bond has been shown for copper-lithium and silver-lithium compounds [9]. Insolubility of the compound suggests a polymeric structure.

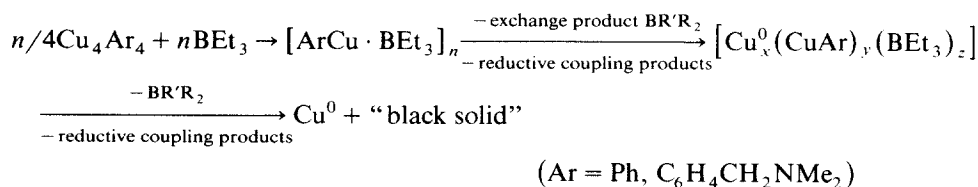
We propose the polymer structure shown in Fig. 5 for the CuAr·BPh-9-BBN complex with copper and boron atoms bonded via aromatic carbon bridges. It is known that copper atoms bonded to carbon have linear C–Cu–C coordination. The next bits of the polymer chain, e.g. the species containing a boron atom bonded to two aromatic ligands and a bicyclic C₈H₁₄ ring has also been synthesized [13].

Fig. 5. Proposed structure of polymeric [(C₆H₄CH₂NMe₂-2)Cu·BPh-9-BBN]_n.

Conclusions

The reaction of CuPh and Cu₄Ar₄ with BEt₃ and BPh-9-BBN in polar solvents were investigated. In the reaction with BEt₃ the thermally unstable intermediates decompose at the reaction temperature with the formation of Cu⁰. From the reaction of Cu₄Ar₄ with BPh-9-BBN the intermediate complex ArCu · BPh-9-BBN was isolated and decomposed thermally at 353 K. The reactions investigated show certain analogies. In these reactions the products containing copper, boron and organic species bonded at various stoichiometric ratios were separated. It seemed that the reactions of CuPh and Cu₄Ar₄ with BEt₃ proceed similarly as the reaction of Cu₄Ar₄ with BPh-9-BBN, but in this case the ethyl ligands do not stabilize the intermediate ArCu · BEt₃ complex and therefore a decomposition process via intramolecular rearrangement occurs immediately. It can be concluded that the decomposition is rather a consequent reaction than a side reaction since arylcopper does not decompose at the observed temperatures. The boron compounds BR'R₂ are released from the polymer during the reaction course. The Cu/B ratio rises gradually, finally giving "black solids" without traces of boron. The second stage of the reaction pathway is very similar to the thermal decomposition process of ArCu · BPh-9-BBN. In the presence of THF the decomposition reaction is favoured since the strong donor is able to break a structure of the intermediate polymer.

Most probably the reaction of Cu₄Ar₄ with BEt₃ proceeds via the following reaction scheme:



Experimental

All experiments were carried out under deoxidized and dried argon. BF₃ · OEt₂ (Fluka A.G., Buchs S.G.) was distilled under argon. Commercially available BEt₃ in hexane (Aldrich) or BEt₃ prepared at the Chemical Faculty of the Technical University in Płock were used. BPh-9-BBN was synthesized according to the modified method reported elsewhere [14], but phenyllithium isolated from the reaction: PhI + BuLi → PhLi + BuI was used instead of a PhLi/LiBr mixture, (BArPh-9-BBN)Li · OEt₂ was prepared as described in ref. 13. PhCu was synthesized in the sequence of reactions described in ref. 11 and 15; Cu₄Ar₄ was obtained by the method reported by Noltes et al. [17].

The amount of copper was established after digesting the sample with diluted nitric acid [18]. The amount of boron was found after oxidative hydrolysis by titration with NaOH in the presence of mannitol.

IR spectra were run on a Perkin-Elmer 527 spectrometer in Nujol mull. ¹H NMR spectra were recorded on JNM-100-H(JEOL) and Tesla 80 MHz spectrometers.

Reaction of Cu₄Ar₄ with BPh-9-BBN (Exp. 9, Table 1). To a solution of BPh-9-BBN (0.495 g, 2.5 mmol) in 15 ml of Et₂O a solution of Ar₄Cu₄ (0.483g, 2.45 mmol) in 50 ml of Et₂O was added dropwise. Precipitation of a yellow solid was

observed immediately after the addition of the first drops of the Cu_4Ar_4 solution. After 3 h the solid was decanted at 195 K and 0.151 g of the yellow solid (a) (Table 1) was separated. Analysis: Cu, 20.19%; B, 3.28%. The remaining reaction mixture was concentrated and 0.119 g of a yellow solid (b) was separated. Analysis: Cu, 18.57%; B, 2.88%.

Decomposition of $\text{ArCu} \cdot \text{BPh-9-BBN}$. A sample of $\text{ArCu} \cdot \text{BPh-9-BBN}$ (0.638 g) was placed in a Schlenk tube and heated for 8 h at 353 K in the solid state. Then 20 ml of Et_2O was added and stirred with the reaction mixture for another 3 h. The ethereal solution was centrifugated and a black solid separated, then active coal was added and the solution became clear. After repeated concentration and dilution BAr-9-BBN and ArAr were separated. From the oily residue ArH was distilled off by microscale distillation. The amount of boron was established for every sample. For all compounds ^1H NMR and IR spectra were run and compared with standards. The black solid was washed four times with ethyl ether, dried under vacuum and the amount of copper was found. Boron proved to be absent.

Acknowledgement

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