Journal of Organometallic Chemistry, 85 (1975) 105—114
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS AND CHARACTERIZATION OF ARYLCOPPER COMPOUNDS CONTAINING THE METHOXY OR DIMETHYLAMINO GROUP AS A BUILT-IN LIGAND*

G. VAN KOTEN, A.J. LEUSINK and J.G. NOLTES
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)
(Received August 9th, 1974)

Summary

The synthesis and isolation of 2,6-dimethoxy-, 2,4,6-trimethoxy-, 2-(dimethylamino)- and 4-(dimethylamino)-phenylcopper are described. The dimethylamino-substituted phenylcopper compounds form complexes with cuprous bromide.

In the case of insoluble compounds a polymeric structure is proposed in which each aryl group bridges two copper atoms by 2e—3c bonds with additional interchain Cu—N (or Cu—O) coordination.

Introduction

Phenylcopper, which is insoluble in the common organic solvents, has limited thermal and oxidative stability [2]. Recently we have described the synthesis [3, 4] and structural characterization [1] of some arylcopper compounds containing the Me_2NCH_2 group as a built-in ligand. These compounds, which are hydrocarbon-soluble, display greatly increased thermal stability. Physico-chemical studies (X-ray, mass spectrometry, NMR and molecular weight determinations) revealed a tetranuclear cluster structure in solution, in the vapour and in the solid, with multicenter bonded aryl groups and very short Cu—Cu distances of 2.38 Å [1, 5].

As part of a study of the influence of built-in ligands in arylcopper compounds on the stability of the Cu—C bond, we have investigated arylcopper compounds containing built-in ligands the heteroatom of which is directly bound to the aryl nucleus. It must be expected that the influence of such ligands on the Cu—C bond will be more complex than that of a CH_2NMe_2 group. In addition to coordinative effects, electronic effects (mesomeric or inductive) exerted by the heteroatom through the ring system on the Cu—C bond will also be an imported factor. The influence of electronic effects on the stability as well as the

* Part XII in the series of publications dealing with Group IB organometallic compounds. For part XI see ref. 1.

aggregation state of arylcopper compounds is illustrated by a comparison of the *ortho*- and *meta*-trifluoromethyl-substituted phenylcopper compounds, i.e. *o*-$CF_3C_6H_4Cu$ tetramer [6], m.p. 200-205° (dec.) and *m*-$CF_3C_6H_4Cu$ octamer [7], m.p. 158° (dec.).

The present paper describes the synthesis of some methoxy- and dimethylamino-substituted phenylcopper compounds*.

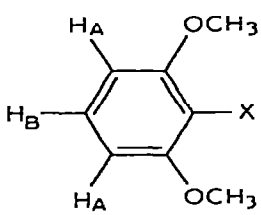
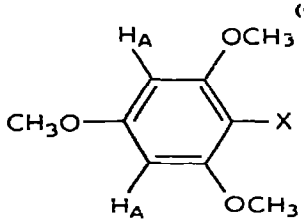
Results

Methoxy-substituted phenylcopper compounds

Reaction of 2,6-dimethoxyphenyllithium (I) with an equimolar amount of cuprous bromide in ether at 0° resulted in the formation of an ether- and benzene-insoluble grey to grey-black solid, which was isolated in 75 to 93% yield. Elemental analysis (C, H, Cu and Br, see Table 1) of the solids isolated from a series of preparations, revealed a composition $CuC_8H_9O_2 \cdot xCuBr \cdot yC_6H_6$ [$0 \leqslant x$ (or y) < 0.3]. Owing to its insolubility in ether and hydrocarbon solvents

TABLE 1

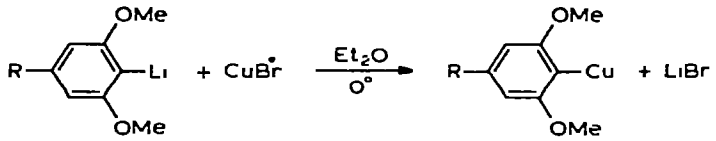
NMR DATA FOR THE METHOXY-SUBSTITUTED PHENYLCOPPER COMPOUNDS AND THEIR PARENT ARENES

Compound	δ (ppm)[a]					Solvent
	2,6-OCH_3	4-OCH_3	H_A	X	H_B	
						
X = H	3.64 (s, 6H)		6.58 (m, 2H)	6.63 (s,br, 1H)	7.20 (2xd, 1H) $J_{A,B} \approx 8$ Hz	C_5D_5N
(III), X = Cu[b]	4.03 (s, 6H)		6.60 (d, 2H)		7.14 (2xd, 1H) $J_{A,B} \approx 8$ Hz	C_5D_5N
						
X = H	3.36 (s, 9H)		6.22 (s, 3H)			C_6D_6
(IV), X = Cu	3.85 (s, 6H)	3.32 (s, 3H)	6.04 (s, 2H)			C_6D_6

[a] Down-field from TMS internal; s, singlet; d, doublet. [b] Singlet at δ 7.35 ppm (C_6H_6): mol. ratio C_6H_6/RCu ≈ 0.16/1.

* For a preliminary account see ref. 8.

compound III could not be obtained pure. Cuprous bromide is most probably present as a contaminant and not in a complexed form.



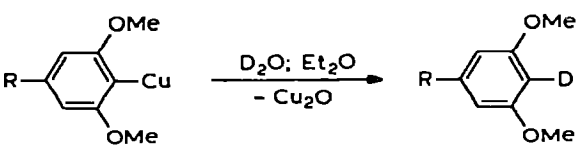
(I), R = H
(II), R = OMe

(III), R = H
(IV), R = OMe

By the same route 2,4,6-trimethoxyphenylcopper (IV) (60-70% yield, cream coloured) was prepared. In contrast with the high insolubility of the dimethoxy compound III, the trimethoxy derivative IV appeared to be soluble in benzene, and thus could be purified by recrystallization.

Proof for the identity of III and IV was obtained from their ^{1}H NMR spectra using pyridine-d_5 (for III) or benzene-d_6 (for IV) as a solvent (see Table 1). The proton resonances belonging to the *ortho*-OCH_3 groups are shifted downfield (0.4-0.5 ppm) with respect to those of the parent arenes. This observation contrasts with the highfield shift of the *ortho*-OCH_3 resonance found in the ^{1}H NMR spectra of 2-methoxyphenylcopper [9]. The resonances due to the 4-OCH_3 group in IV and the parent arene are found at almost the same position. This indicates that in solution the 4-methoxy group is not involved in coordination with copper.

Both III and IV afforded the expected 2-deuterio derivatives upon reaction with D_2O.



(III), R = H
(IV), R = OMe

(V), R = H (at least 144h; 75% yield)
(VI), R = OMe (24h; 80% yield)

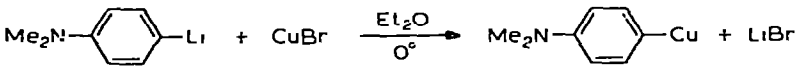
The strikingly different properties of both organocopper compounds, viz.: *i*, III insoluble and IV very soluble in ether and hydrocarbon solvents; *ii*, different deuterolysis rates (see eqn.); *iii*, III rather stable in air vs. a rapid decomposition in air of IV, illustrate the pronounced influence of the introduction of a methoxy group at the 4-position in 2,6-dimethoxyphenylcopper (III).

It is interesting to note that contrary to the CH_2NMe_2-substituted phenylcopper compounds [3, 4] 2,4,6-trimethoxyphenylcopper (IV) does not form a complex with cuprous bromide*; from an equimolar mixture of CuBr and IV in benzene, which was stirred at room temperature during 40 h, the organocopper (IV) as well as CuBr were recovered quantitatively.

* Recently, Camus and Marsich [10] have reported the isolation of 2-methoxyphenylcopper which is benzene-soluble and rather thermostable (dec. at 150°). It was stated that the yield was about 20%, but very dependent on the experimental conditions. We have observed that 2-methoxyphenylcopper forms readily complexes with cuprous bromide and that this complex-formation interfers seriously with attempts to isolate the organocopper in the pure state [12].

Dimethylamino-substituted phenylcopper compounds

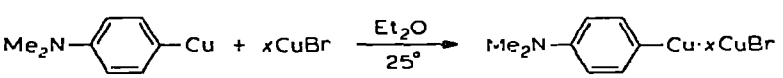
a. 4-(Dimethylamino)phenylcopper. 4-(Dimethylamino)phenylcopper (VIII) was synthesized as follows:



(VII) (VIII)

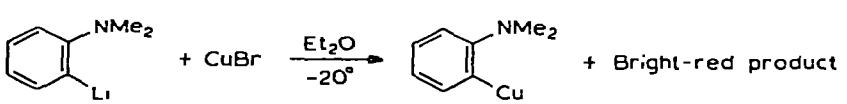
The addition of the first quantity of the organolithium solution to the cuprous bromide suspension, caused a colour change from white to purple. After completion of the addition of VII (1/1 molar ratio) a cream coloured precipitate was present, which was isolated by filtration (88% yield). This product, which appeared to be extremely sensitive towards oxidation and hydrolysis, consisted of almost pure 4-(dimethylamino)phenylcopper (VIII). The isolation of 4-deuterio-*N*,*N*-dimethylaniline (IX) (72% yield) from the reaction of VIII with D_2O confirmed this.

The colour change of the CuBr suspension at VII/CuBr ratios lower than 1 is ascribed to complex-formation of the organocopper formed with the excess of cuprous bromide present. This view is supported by the isolation of purple solids (in about 90% yield) from the reaction of VII with a slight excess of CuBr as well as from the 1/1 reaction of VIII with CuBr. This complex-formation increases the stability of the copper—carbon bond in VIII towards hydrolysis and oxidation. Moreover, the thermal stability depends on the value of x; i.e. decomposition at 117-120° for VIII (x = 0); at 136-140° for X (x = 0.36) and at 170° for XI (x = 1.09). However, since the organocopper compound (VIII), CuBr, as well as the complexes X and XI are highly insoluble in ether and hydrocarbon solvents it is not known whether all CuBr in X and XI is present in the complexed form.



(VIII) (X), x = 0.36
(XI), x = 1.09

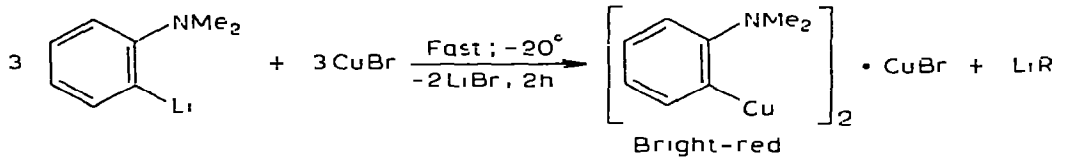
b. 2-(Dimethylamino)phenylcopper. Reaction of 2-(dimethylamino)phenyllithium (XII) with cuprous bromide [addition of CuBr to a solution of XII] afforded ether- and hydrocarbon-insoluble, impure 2-(dimethylamino)phenylcopper (XIII) (60% yield) and a benzene-soluble red-coloured product (19% yield). The purification of XIII obtained in this way was hampered by the presence of insoluble side-products.



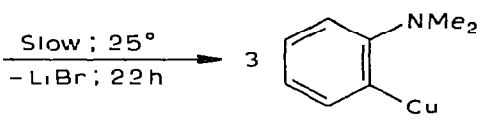
(XII), RLi (XIII), RCu

A closer examination of this reaction revealed that reversed addition of both reagents, i.e. addition of XII to a suspension of cuprous bromide in ether,

primarily gives rise to the formation of the 2/1 complex of XIII with CuBr* and that this complex (2 CuR·CuBr) is then converted in a slow reaction into 2-(dimethylamino)phenylcopper (XIII). From this reaction almost pure 2-(dimethylamino)phenylcopper was obtained in 72% yield.



Bright-red

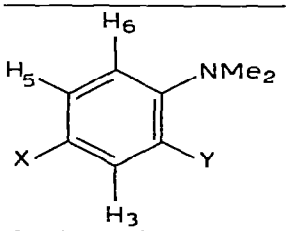


Cream-coloured (XIII)

In contrast to 4-(dimethylamino)phenylcopper, XIII displays high thermal and hydrolytic stability. In moist air the cream colour turns slowly to green. The reaction with D_2O proceeded very slowly; total decomposition requires 7 days [86% yield of 2-deuterio-*N*,*N*-dimethylaniline (XIV)]. TGA analysis of XIII revealed that slow decomposition starts at 109° (heating rate 3°/min; at 194° about 5% loss of weight); fast decomposition at 207-215°.

TABLE 2

NMR DATA[a] FOR DIMETHYLAMINO-SUBSTITUTED PHENYLCOPPER COMPOUNDS

Compound	δ (ppm)					
	NCH_3	H_2	H_6	H_3	H_5	H_4
						
Y = H_2; X = H_4	2.68 (s, 6H)	6.70 (m, 2H)			7.24 (m, 2H)	≈ 6.75 (m, 1H)
(VIII) Y = H_2; X = Cu	2.70 (s, 6H)	6.71 (d, 2H)[b]			8.22 (d, 2H)	
(XIII), Y = Cu; X = H_4	2.92 (s, 6H)		6.54 (d, 1H)[c]	8.91 (d,br, 1H)[d]	7.01 (tr of d, 1H) and ≈ 7.2[e]	

[a] TMS internal; ambient temperature; in pyridine-d_5: [b] $J_{2,3} = J_{5,6} \approx 8$ Hz. [c] $J_{5,6} \approx 8$ Hz. [d] $J_{3,4} \approx 7$Hz. [e] Multiplet (H_4 or H_5) partly masked by $C_5D_{5-x}H_xN$ resonances.

* An X-ray structure determination of this complex $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ has been reported [11]. For further details see ref. 12.

c. NMR spectra of VIII and XIII. The NMR data of the 2- and 4-dimethylamino-substituted phenylcopper compounds VIII and XIII, dissolved in pyridine-d_5, are listed in Table 2. The following observations are made:

i. For 4-(dimethylamino)phenylcopper (VIII; Y = H_2 and X = Cu) both the protons H_2 and H_6 (*meta* to the Cu—C bond) and the NCH_3 protons are found at almost the same chemical shift values as in the spectrum of the parent arene, *N,N*-dimethylaniline. Apparently, only the protons H_3 and H_5 (*ortho* to the Cu—C bond) which as compared with the arene appear about 1 ppm down-field experience the anisotropy of the metal—carbon bond.

ii. For 2-(dimethylamino)phenylcopper (XIII; Y = Cu and X = H_3), again, the protons which reside at the *ortho* positions with respect to the Cu—C bond are shifted down-field; i.e. H_3 about 1.7 ppm and the NCH_3 protons about 0.2 ppm. This additional down-field shift of H_3 ($\approx$ 0.7 ppm) as compared with H_3 in VIII can be explained on the basis of copper being in close proximity with the Me_2N group.

Discussion

In contrast with the general *solubility* of the 2-CH_2NMe_2-substituted phenylcopper compounds most of the compounds described here are *insoluble* in non- or weakly-coordinating solvents. Exceptions are the benzene-soluble 2/1 complex of 2-(dimethylamino)phenylcopper with cuprous bromide $(2\text{-}Me_2NC_6H_3)_3Cu_6Br_2$ [11,12] and 2,4,6-trimethoxyphenylcopper (IV). The structure of the latter compound is unclear at this moment; no conclusive molecular weight data could be obtained (values for *n* between 5 and 7 were measured).

The collection of data which could give information about the structure of the other compounds is hampered by their high insolubility. The insolubility of phenylcopper has been used by several authors as an argument for a polymeric structure based upon the interaction of filled copper *d*-orbitals with anti-bonding π-orbitals of the phenyl nucleus [13]. However, this proposal was made at a time when X-ray structural information concerning arylcopper compounds was not available. Based on the results of recent X-ray structure determinations [5,11,14], a plausible alternative for the above proposal seems a polymeric structure in which each phenyl group bridges two copper atoms by two electron-three center bonds as pictured in Fig. 1. In this proposed structure the copper atoms are assumed to be two-coordinate with an almost linear arrangement of the C_{Ph}—Cu—C_{Ph} bond. This stereochemistry around copper in organocopper compounds has precedents

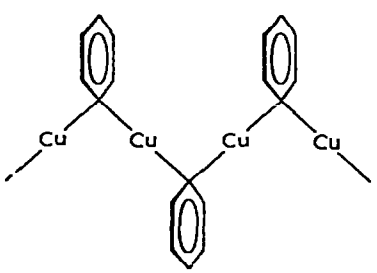
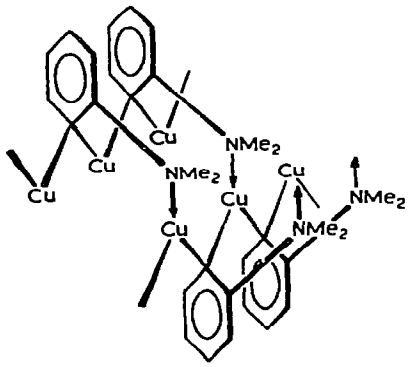


Fig. 1. Proposed structure for phenylcopper coordination polymer.



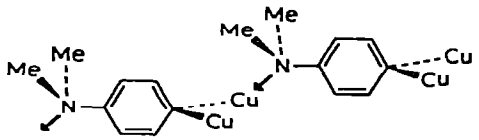


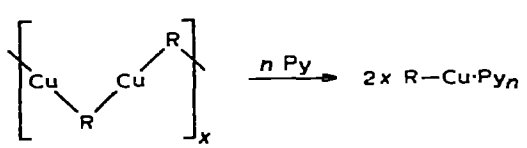
Fig. 2. Proposed structure for 2-(dimethylamino)phenylcopper coordination polymer.
Fig. 3. Proposed structure for 4-(dimethylamino)phenylcopper coordination polymer.

in the structure of $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ [11], of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ [15] and of $(Me_3SiCH_2Cu)_4$ [14].

This proposal may serve as a basis for the structure of the insoluble and presumably polymeric methoxy- and dimethylamino-substituted phenylcopper derivatives. For $2\text{-}Me_2NC_6H_4Cu$ (XIII) and $2,6\text{-}(MeO)_2C_6H_3Cu$ (III) additional "interchain" Cu—N- (or Cu—O) coordination is assumed which results in a network-structure as visualized in Fig. 2. In this type of structure the copper atoms are three-coordinate. Three-coordination of copper involving two Cu—C electron-deficient bonds and one Cu—N coordination bond has precedents in the structures of $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ (equatorial copper atoms [11]) and of $(5\text{-Me-}2\text{-}Me_2NCH_2C_6H_3)_4Cu_4$ [1,5].

A similar network-structure is proposed for 4-(dimethylamino)phenylcopper (VIII), see Fig. 3. The presence of the dimethylamino-ligand in the 4-position will give rise to a less compact network, resulting in a smaller steric shielding of the Cu—C bond. This might explain the difference in oxidative and hydrolytic stability between the 2- and 4-substituted derivatives VIII and XIII [solid $(4\text{-}Me_2NC_6H_4Cu)_n$ is much less stable than solid $(2\text{-}Me_2NC_6H_4Cu)_n$].

It is noteworthy that phenylcopper and the polymeric organocopper compounds dissolve in strongly coordinating solvents such as pyridine. The polymeric structure breaks down as a result of coordination of the solvent to copper; i.e. the aryl groups change from a state of electron-deficient bonding into a state of electron-complete bonding*.



* For a more general discussion of the complex-forming properties of arylcopper compounds see ref. 12.

Experimental (with Mr. C.A. Schaap)

General

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

^{1}H NMR spectra, which were run by Mrs. L. van der Grift-Veldstra were recorded on a Varian Associates HA-100 NMR spectrometer. IR spectra, which were run by Mrs. H. de Ridder-Alberda and Mrs. G.M. Bijlsma-Kreuger, were recorded on a Grubb-Parsons Spectromaster. Elemental analyses were carried out under the supervision of Mr. W.J. Buis in the Analytical Department of this Institute.

Methoxyphenyllithium compounds (I) and (II)

A solution of 1,3-dimethoxy- or 1,3,5-trimethoxy-benzene (10 mmol) in diethyl ether (15 ml) was added to a solution of butyllithium (10 mmol) in ether (28 ml)/hexane (7 ml). The mixture was stirred at room temperature for 70 h. The resulting mixtures, containing 2,6-dimethoxy- (I) or 2,4,6-trimethoxyphenyllithium (II), were used directly for the reactions with cuprous bromide.

Reactions with D_2O. The solution containing I or II, respectively was added to an ether (20 ml)/D_2O (2 ml) mixture. The mixture was stirred for 3 h then filtered and the filtrate dried over $MgSO_4$. Concentration afforded a yellow oil in the case of I and an almost white solid in that of II. NMR spectroscopy (see ref. 16 for the δ values) revealed the exclusive formation of the respective 2-deuterio compounds V and VI. IR (neat) of V; characteristic absorptions at 785 s and 733 s cm^{-1}.

2,6-Dimethoxyphenylcopper (III)

Cuprous bromide (100 mmol) was added at 0° to a solution of 2,6-dimethoxyphenyllithium (I) in ether (350 ml)/hexane (54 ml). After stirring for 3 h at 0° and for 1 h at room temperature the black suspension was filtered. The solid was extracted with ether (4 × 40 ml; removal of LiBr) and with benzene (4 × 15 ml) yielding a grey-black ether- and hydrocarbon-insoluble solid (IIIa) (yield 92.5%; dec. temp. 185-189°). (Found: C, 41.0; H, 4.1; Br, 6.8; Cu, 29.8. $C_8H_9O_2Cu \cdot 0.23\ CuBr \cdot 0.16\ C_6H_6$ calcd.: C, 43.7; H, 4.08; Br, 7.46; Cu, 31.75%.)

In another preparation extraction with benzene was omitted. A greyish-black solid IIIb was isolated. (Found: C, 46.3; H, 4.7; Br, 0.0; Cu, 32.5. $C_8H_9Cu \cdot 0.06\ Cu$ calcd.: C, 46.98; H, 4.44; Cu, 32.93%.) NMR spectrum identical with that of IIIa (See Table 1).

Reaction with D_2O. IIIa (3.5 mmol) in Et_2O (40 ml)/D_2O (2 ml), 144 h, room temperature; 75% of V and 80% of C_6H_6 (GLC). NMR data see ref. 16.

2,4,6-Trimethoxyphenylcopper (IV)

Cuprous bromide (19.5 mmol) was added at −20° to a solution of 2,4,6-trimethoxyphenyllithium (II) (19.5 mmol) in ether (85 ml)/hexane (15 ml). During the reaction a cream-coloured solid precipitated from the reaction mixture. This solid was filtered off, extracted with ether (3 × 20 ml) and dried in vacuo. Recrystallization from benzene afforded a cream-coloured solid IV in 65% yield.

Dec.temp. 195-200° [white crystals of 1,3,5-trimethoxybenzene, m.p. 56° (lit. m.p. 54-55°) were formed]. (Found: C, 48.4; H, 5.1; Cu, 25.6. $C_9H_{11}O_3Cu \cdot 0.16$ C_6H_6 calcd.: C, 49.19; H, 4.96; Cu, 26.13%.) NMR data see Table 1. IR (KBr) cm^{-1}: 943 w, 933 w, 911 vw, 818 (vbr), 677 w (benzene).

Reaction with D_2O. IV (1.90 mmol) in ether (10 ml)/D_2O (2 ml), 24 h, room temperature: 81% of VI and 73% of C_6H_6 (GLC). NMR data see ref. 16.

Interaction with CuBr. IV (2.10 mmol)/CuBr (2.10 mmol) in benzene (30 ml), 40 h, room temperature. The cream-coloured precipitate was filtered off and extracted with benzene. Quantitative recovery of CuBr (Found: Cu, 43.0. CuBr calcd.: Cu, 44.3%.) From the benzene extract pure IV (according to IR) was isolated quantitatively.

4-(Dimethylamino)phenylcopper (VIII)

A solution of 4-bromo-*N,N*-dimethylaniline (30 mmol) in ether (45 ml) was added to chips of lithium (64.5 mat) in ether (30 ml). After addition ($\frac{1}{2}$ h) of the bromo derivative the solution was stirred for another 2 h. The reaction mixture was filtered. A 2 ml sample of the filtrate was hydrolyzed with water (2 ml) and the amount of *N,N*-dimethylaniline determined by GLC (see synthesis of XIII). Calculated yield of VII 80%.

The remaining solution of VII was added at 0° to a suspension of CuBr (24 mmol) in ether (40 ml). After stirring for 2 h at 0° and for $1\frac{1}{2}$ h at room temperature the cream-coloured solid was filtered off, extracted with ether (3 × 20 ml) and then dried. VIII remained in 88% yield. (Found: C, 50.0; H, 5.4; Br, 1.2; Cu, 33.2; N, 7.3. $C_8H_{10}NCu \cdot 0.03$ CuBr· 0.05 Et_2O calcd.: C, 51.37; H, 5.52; Br, 1.25; Cu, 34.13%; N, 7.31. NMR data see Table 2. IR (Nujol) cm^{-1}: 1608 s(sh), 1590 vs, 1449 s, 1266 w, 1235 m, 1208 m, 1176 m, 1130 w, 1068 w, 1040 m, 1000 w, 950 m, 806 m(sh), 800 s, 750 m, 720 w, 690 w, 530 w(br), 520 w(vbr).

Reaction with CuBr. Solid VIII (10 mmol) was added at room temperature to a suspension of CuBr (10 mmol) in ether (30 ml). The resulting reaction mixture containing a purple-red solid was stirred for 24 h. Filtration followed by extraction of the precipitate with benzene afforded a purple-red solid XI (89% yield). (Found: C, 27.6; H, 3.1; Br, 24.9; Cu, 37.6; N, 4.0. RCu· 1.09 CuBr calcd.: C, 28.25; H, 2.96; Br, 25.61; Cu, 39.05%; N, 4.12.) IR (KBr)cm^{-1}: 1600 s(sh), 1582 s, 1504 s, 1445 s, 1264 w, 1235 m, 1205 s, 1175 m, 1130 w, 1064 w, 1033 m, 1012 m, 990 m, 943 m, 806 s(sh), 800 s, 796 (sh), 752 m, 693 m, 536 m(vbr).

Reaction of XI with D_2O. XI (3.74 mmol) in benzene (10 ml)/D_2O (1 ml), room temperature, 48 h: 72% of IX. IR (IX) (neat)cm^{-1}: ν(C—D) 2268 (2294 and 2283 sh). NMR (CCl_4) δ ppm: 2.82 (s, 6H, NCH_3), 6.58 (m, 2H, $H_{2,6}$), 7.10 (m, 2H, $H_{3,5}$).

2-(Dimethylamino)phenylcopper (XIII)

A solution of 2-bromo-*N,N*-dimethylaniline (60 mmol) in ether (60 ml) was added in $1\frac{1}{2}$ h to 0.128 g-atom of metallic lithium in ether (75 ml) containing 1.8534 g of n-decane as internal standard. The resulting mixture was refluxed for $\frac{3}{4}$ h and was subsequently filtered. The amount of organolithium in the filtrate was determined by GLC analysis (decane: *N,N*-dimethylaniline ratio) of a hydrolyzed sample of this solution.

The solution of 2-(dimethylamino)phenyllithium (XII: 51 mmol) was added at −20° to a suspension of cuprous bromide (51 mmol) in ether (120 ml). The resulting red mixture was stirred at −20° for ¾ h and for an additional hour at room temperature. After addition of benzene (200 ml) about 80% of the ether was removed at low pressure. The remaining mixture was stirred for 16 h at room temperature. The orange precipitate was filtered off and extracted with benzene (3 × 20 ml) and with ether (4 × 20 ml, removal of LiBr), after which it was dried in vacuo. The resulting orange-white solid was further purified by repeated extraction with benzene and pentane. Solid, cream-coloured XIII was obtained (72% yield). (Found: C, 52.0; H, 5.4; Cu, 33.6; N, 7.6. $C_8H_{10}NCu$ calcd.: C, 52.30; H, 5.49; Cu, 34.59; N, 7.62%.) NMR data see Table 2. IR*(nujol)cm^{-1}: 1572 m, 1560 (sh), 1540 w, 1479 m, 1429 w, 1412 w, 1400 w, 1368 w, 1345 w, 1299 w, 1253 (sh), 1242 w, 1225 w, 1210 w, 1165 (sh), 1160 m, 1115 w, 1095 w, 1052 m, 1043 m, 1000 m, 945 m, 932 w, 835 w, 760 (sh), 752 s, 728 (sh), 718 s, 558 w, 536 w, 500 s, 462 m, 315 w.

Reaction of VIII with D_2O. XIII (3.38 mmol) in benzene (10 ml)/D_2O (1 ml) room temperature, 7 days, 86% yield of XIV. IR (neat): γ(C—D) 2283 cm^{-1} and in the 900-600 cm^{-1} region: 867 w, 844 w, 781-718 vs(br), 625 s.

Acknowledgement

This research was supported by the International Copper Research Association, Inc., New York.

References

1 G. van Koten and J.G. Noltes, J. Organometal. Chem., 84 (1974) 129.
2 G. Costa, A. Camus, L. Gatti and N. Marsich, J. Organometal. Chem., 5 (1966) 568.
3 G. van Koten, A.J. Leusink and J.G. Noltes, J. Organometal. Chem., 84 (1974) 117.
4 G. van Koten and J.G. Noltes, J. Organometal. Chem., 84 (1974) 419.
5 J.M. Guss, R. Mason, I. Sotofte, G. van Koten and J.G. Noltes, J. Chem. Soc., Chem. Commun., (1972) 446.
6 A. Cairncross and W.A. Sheppard, J. Amer. Chem. Soc., 93 (1971) 247.
7 A. Cairncross, H. Omura and W.A. Sheppard, J. Amer. Chem. Soc., 93 (1971) 248.
8 G. van Koten, A.J. Leusink and J.G. Noltes, Inorg. Nucl. Chem. Lett., 7 (1971) 227.
9 A. Baici, A. Camus and G. Pellizer, J. Organometal. Chem., 26 (1971) 431.
10 A. Camus and N. Marsich, J. Organometal. Chem., 14 (1968) 441.
11 J.M. Guss, R. Mason, K.M. Thomas, G. van Koten and J.G. Noltes, J. Organometal. Chem., 40 (1972) C79.
12 G. van Koten and J.G. Noltes, to be published.
13 E.g., G. Costa, A. Camus, N. Marsich and L. Gatti, J. Organometal. Chem., 8 (1967) 339.
14 J.A.J. Jarvis, B T. Kilbourn and R. Pearce, J. Chem. Soc., Chem. Commun., (1973) 475.
15 G. van Koten and J.G. Noltes, J. Chem. Soc., Chem. Commun., (1972) 940.
16 A.J. Leusink, G. van Koten and J.G. Noltes, J. Organometal. Chem., 56 (1973) 379.

* Recorded on a Perkin—Elmer 577 Grating Infrared Spectrometer.