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REACTION OF DIARYLZINC COMPOUNDS WITH COPPER(I) SALTS. SYNTHESIS AND CHARACTERIZATION OF ARYLCOPPER(I) COMPOUNDS

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Summary

The reaction of diarylzinc compounds with copper(I) salts is an excellent way of preparing stable arylcopper compounds in quantitative yields. These compounds have been characterized by IR, and by ^1H and ^{13}C NMR spectroscopy. Cryoscopic molecular weight determinations show phenylcopper to be polymeric and 2-methylphenylcopper and 2,6-dimethylphenylcopper to be tetrameric in benzene. The compounds are believed to contain aryl groups bridging two copper atoms. Evidence is presented for rotation of these aryl groups around the C(1)—C(4) axis.

Introduction

The first reported synthesis and isolation of phenylcopper was in 1923 [1]. However, the tendency of phenylcopper to form complexes with metal salts (e.g. LiX and MgX_2) hampered the isolation of pure products (cf. the paper of Costa et al. on the preparation of phenylcopper [2]). Moreover, we have observed that organo-lithium and -magnesium reagents cause partial reduction of the copper salts used as starting materials. We now describe a new and easy synthesis of phenylcopper, 2-methylphenylcopper, and 2,6-dimethylphenylcopper using diarylzinc compounds as arylating agents.

Results and discussion

When finely divided Cu^ICl or Cu^IBr is stirred with an ether solution of diphenylzinc, bis(2-methylphenyl)zinc or bis(2,6-dimethylphenyl)zinc in a 1/2 molar ratio (8 h at —10°C), the corresponding arylcopper compounds are formed as colourless solids in quantitative yields:

$$Ar_2Zn + CuX \xrightarrow[-10^\circ C]{Et_2O} ArCu\downarrow + [ArZnX]$$

(X = Cl or Br, Ar = phenyl (I), 2-methylphenyl (II), 2,6-dimethylphenyl (III))

After washing with ether and drying in vacuo at −10°C the compounds were obtained analytically pure: Analyses: I found: C, 50.8; H, 3.8; Cu, 45.0 C_6H_5Cu calcd.: C, 51.26; H, 3.56; Cu, 45.18%. II found: C, 54.3; H, 4.6; Cu, 41.1. C_7H_7Cu calcd.: C, 54.35; H, 4.57; Cu, 41.08%. III found: C, 56.6; H, 5.1; Cu, 37.6. C_8H_9Cu calcd.: C, 56.98; H, 5.34; Cu, 37.68%.

The thermal stability of the compounds was measured by DTA at a heating rate of 5°/min; decomposition temperatures: I, 99°C; II, 134°C; III, 191°C. It thus appears that the thermal stability rises considerably with the degree of *o*-methyl substitution. Cryoscopic molecular weight determinations in benzene showed phenylcopper to be polymeric ($n > 10$), and 2-methylphenylcopper and 2,6-dimethylphenylcopper to be tetrameric ($n = 3.97$ and 4.07, resp.) *. All the molecular weights were concentration independent.

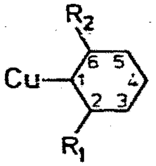
The IR spectra of phenylcopper (I) and 2-methylphenylcopper (II) were identical with those reported by Camus et al. [2,3]. The spectrum of 2.6-dimethylphenylcopper (III) shows the characteristic absorptions ascribed to the substituent-sensitive vibration modes of the aryl group [4]. The Raman spectra show no absorptions in the region where metal—metal vibrations are expected. The NMR data for the compounds are listed in Table 1.

Because of the quadrupole moment of the copper nucleus, no Cu—^{1}H and Cu—^{13}C couplings were detected. The NMR spectra show no concentration dependence.

Four structural possibilities have to be considered for these compounds, viz. one with aryl groups bridging between copper atoms, a second with aryl groups *σ*-bonded to one copper atom and *π*-bonded to other copper atoms, a third in which both types of bonding occur, and a fourth one in which Cu—Cu bonds are also present. The Raman spectra rule out structures in which there is copper—copper bonding. The NMR spectra indicate the presence in each com-

TABLE 1

^{1}H AND ^{13}C NMR SPECTRAL DATA [a] FOR ARYLCOPPER COMPOUNDS AT −30°C (Resonance positions in ppm relative to internal TMS)

	C_6H_5Cu $R^1 = R^2 = H$	C_7H_7Cu [e] $R^1 = CH_3$; $R^2 = H$	C_8H_9Cu [f] $R^1 = R^2 = CH_3$
H(2,6)	7.90 [b]	7.97 [b]	—
H(2,4,5)	7.25 [c]	7.15 [c]	6.95 [c]
C(1)	137.3	139.2 [d]	140.3
C(2)	144.4	154.8	155.1
C(3)	127.5	127.4	124.7
C(4)	131.3	131.2	131.1
C(5)	127.5	124.5	124.7
C(6)	144.4	144.1 [d]	155.1

[a] Deuteriochloroform solution: spectra recorded in toluene-d_8 gave similar results. [b] Estimated mean value of a well-defined doublet. [c] Multiplets. [d] Estimated mean value of a well-defined multiplet. [e] $H(CH_3)$ 2.80 ppm (well-defined multiplet); $C(CH_3)$ 29.1 ppm. [f] $H(CH_3)$ 2.87 ppm; $C(CH_3)$ 29.1 ppm.

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* Note added in proof. Very recently Van Koten et al. [16] reported 2-methylphenylcopper to be tetrameric in benzene.

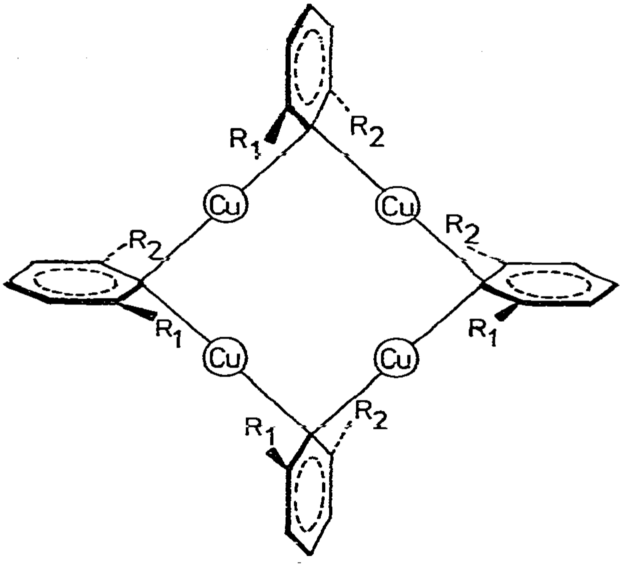


Fig. 1. Proposed structure for 2-methylphenylcopper ($R^1 = CH_3$, $R^2 = H$) and for 2,6-dimethylphenylcopper ($R^1 = R^2 = CH_3$).

pound of only one type of aryl group, and therefore rule out the third possibility. On comparing the ^{13}C NMR spectral shifts of these copper compounds with those of well-known π-complexes of silver(I) salts [5] and of copper(I) salts [6], it is evident that π-interaction of the aromatic system with the copper nuclei can also be ruled out. Thus, our data indicate that aryl groups bridging between two copper atoms, well established in Group IB-chemistry [7—9], must be present in compounds I, II and III.

In view of the spectral data and of the observed high molecular weight our work supports the suggestion of Van Koten [7] that phenylcopper is a coordination polymer containing phenyl groups bridging between two copper atoms. For the tetrameric species II and III we propose a structure as shown in Fig. 1.

In the absence of additional coordinating ligands, each copper atom is linearly coordinated [10]. As a result, in these tetramers the copper atoms are necessarily coplanar. In view of the steric requirements of substituted aryl groups the Cu—C—Cu bond angles will be as large as the flat tetramer allows, i.e. 90°. The NMR spectra of the symmetrically substituted 2,6-dimethylphenylcopper indicate the presence of only one kind of methyl group at all temperatures investigated, which points to a symmetrical structure of the tetramer concerned. In other words, the bridging carbon atoms are situated in the same plane as the copper atoms (cf. the similar structure of $[Me_3SiCH_2Cu]_4$ [11]).

When the aryl groups are non-symmetrical, as in 2-methylphenylcopper, the NMR spectra show that configurational isomerism does occur. Whereas the ^1H and ^{13}C NMR spectra of (I and) III are temperature and concentration independent, the spectra of 2-methylphenylcopper (II) change upon cooling. The ^1H NMR spectrum of the latter (Fig. 2) reveals the existence of several methyl groups at temperatures of —30°C and below.

The ^{13}C NMR spectra (Fig. 3) show rather broad absorptions for all carbon

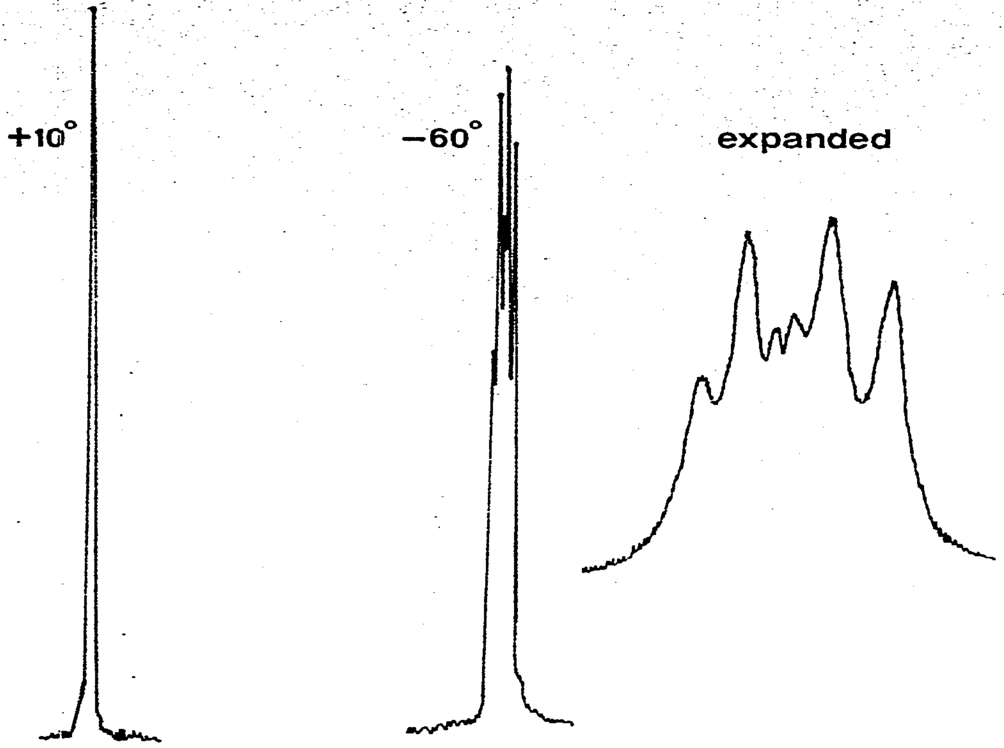


Fig. 2. ^{1}H NMR spectra of 2-methylphenylcopper (methyl-group region).

atoms at 10°C; at temperatures of −30°C and below, the resonances of C(1) and C(6) are split up into multiplets, the other signals remaining rather broad.

Since in none of these spectra was a concentration dependence observed, an intermolecular process is excluded, and the results must be accounted for by an intramolecular process. An earlier suggestion [12] that the multiplet for the methyl group observed in the ^{1}H NMR spectra of 2-methylphenylcopper should

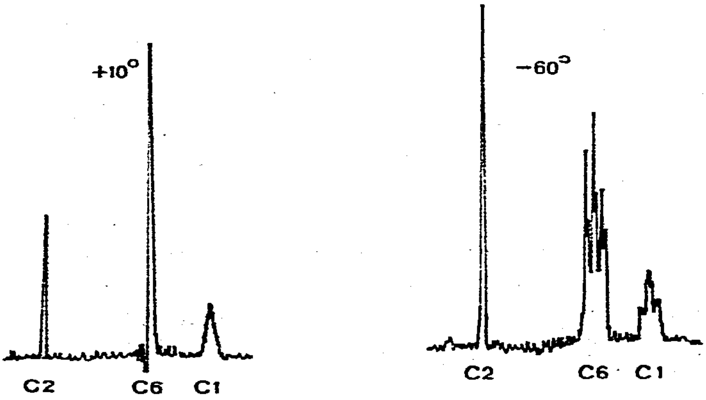
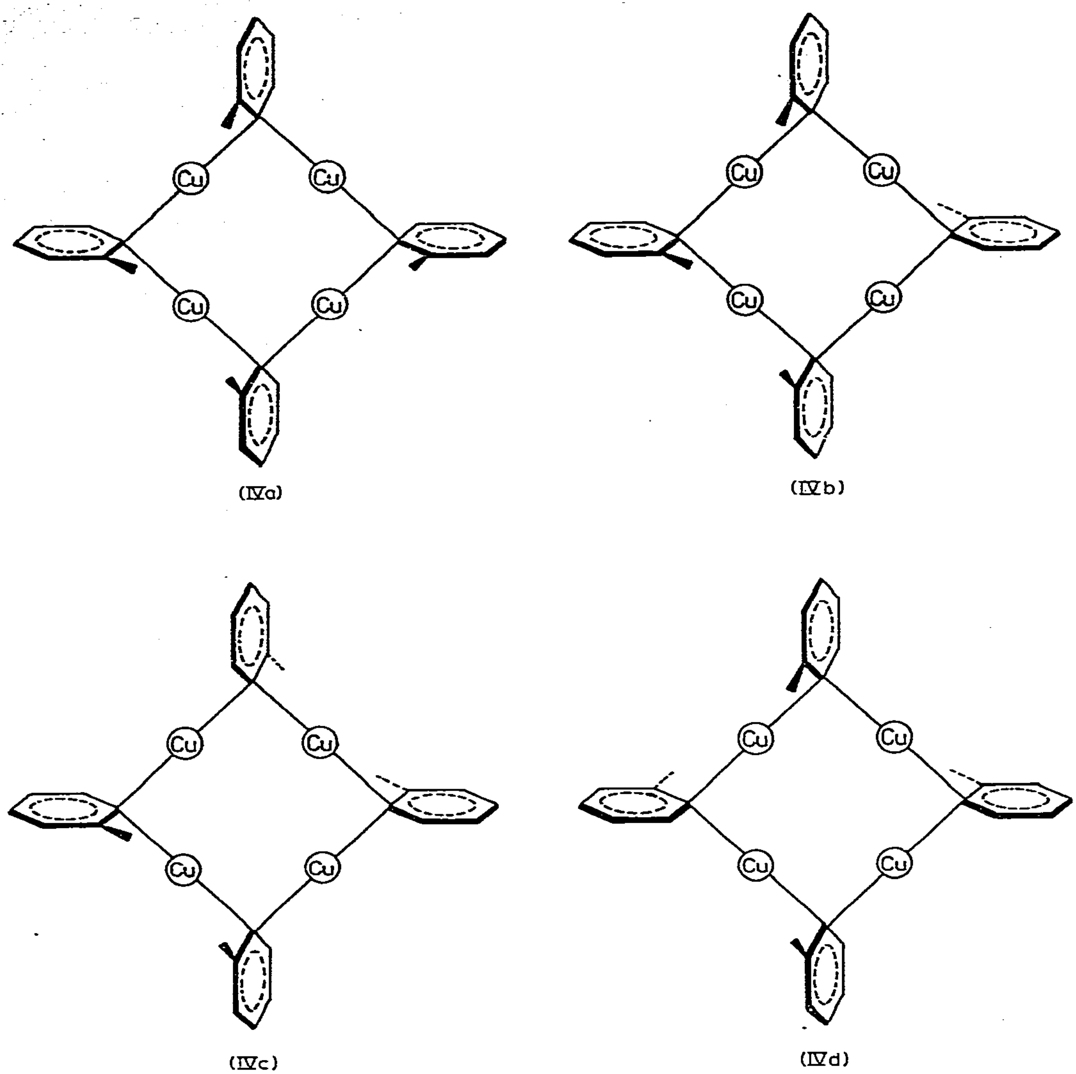


Fig. 3. ^{13}C NMR spectra of 2-methylphenylcopper.



(IVa) (IVb)

(IVc) (IVd)

Fig. 4. Configurational isomers of 2-methylphenylcopper.

be attributed to hindered rotation of the methyl group appears to be incorrect. Our combined ^1H and ^{13}C spectral data indicate that the behaviour of this compound is the result of the existence of several configurational isomers arising from hindered rotation of the aryl group. At 0°C the aryl groups rotate fast enough to cause interconversion of the isomers, leading to an averaged spectrum. At −30°C and below, the rotation around the C(1)—C(4) axis is hindered, resulting in the spectral observation of several species. The presence of different configurational isomers cannot be detected in the case of phenylcopper and 2,6-dimethylphenylcopper owing to the symmetry of the aryl groups. In our opinion the configurational isomers shown in Fig. 4 account for the observed spectra of 2-methylphenylcopper.

We believe this to be the first evidence for rotation of aryl groups which bridge two metal atoms by means of a 2e - 3c bond.

Conclusion

As found earlier for arylation of silver [13] and gold [14], diarylzinc compounds are excellent reagents for the arylation of copper(I) because they lack the reducing effects of aryllithium and arylmagnesium compounds. Moreover, complexation with zinc or copper salts does not occur when diarylzinc compounds are used to synthesize arylcopper compounds.

The NMR spectra indicate that bridging aryl groups rotate around the C(1)—C(4) axis. This conclusion is based on the occurrence of configurational isomerism for the non-symmetrically substituted compound 2-methylphenylcopper, and the absence of such isomerism for the symmetrically substituted compound 2,6-dimethylphenylcopper. We are currently extending this study to other substituted arylcopper compounds to determine the scope of this synthetic route, and to elucidate the structures of the products.

Experimental

General

All experiments were carried out under dry, oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen. NMR spectra were recorded on Varian EM-390 and XL-100/15FT NMR spectrometers using deuteriochloroform as solvent. The IR spectra were recorded on a Perkin-Elmer 457 grating infrared spectrometer using Nujol mulls between KBr disks. The Raman spectra were recorded on a Spectra Physics 700 Raman spectrometer with a Spectra Physics argon ion laser (model 165). Elemental analyses were carried out under the supervision of Mr. W.J. Buis in the Analytical Department of the Institute for Organic Chemistry TNO at Utrecht.

Synthesis of diphenylzinc

A solution of dry $ZnCl_2$ in ether was added dropwise to the Grignard reagent prepared from Mg (12.5 g, 500 mmol) and PhBr (81 g, 515 mmol) in ether until the Gilman test [15] was negative. The reaction mixture was transferred to a separating funnel and added in small portions to an evacuated distillation apparatus fitted with an aircooled condenser. When all solvent was thus removed, Ph_2Zn was destilled into the condenser at a bath temperature of 250—300°C (b.p. 180°C/10^{-4} mmHg), yielding 40.8 g (186 mmol, 74% overall yield) of pure product after washing with pentane (5 × 50 ml).

Synthesis of bis(2-methylphenyl)zinc and bis(2,6-dimethylphenyl) zinc

A solution of $ZnCl_2$ in ether was added dropwise to a Grignard reagent prepared from Mg (12.2 g, 500 mmol) and 2-bromotoluene or 2,6-dimethylbromobenzene (500 mmol) in ether until the Gilman test was negative. All solvent was removed by suction (70°C/1 mmHg) and the residue was extracted exhaustively with benzene. Evaporation of the benzene yielded impure R_2Zn. Crystallisation from toluene gave bis(2-methylphenyl)zinc or bis(2,6-dimethylphenyl)zinc, which was washed with pentane to give analytically pure white crystals in a 60% overall yield.

Synthesis of phenylcopper, 2-methylphenylcopper and 2,6-dimethylphenylcopper

Finely divided Cu^ICl * (0.5 g) was stirred for 8 h at −10°C with an ether solution of diphenylzinc, bis(2-methylphenyl)zinc or bis(2,6-dimethylphenyl)zinc in a 1/2 molar ratio. The corresponding arylcopper compounds were formed as colourless solids in quantitative yields. After washing with ether (4 × 20 ml) and drying in vacuo at −10°C the compounds were obtained analytically pure (95—99% overall yield).

Acknowledgements

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* The reaction mixture had to be stirred for 10 h when CuBr was used.