

Stable Arylcopper Compounds Containing 2-(Dimethylamino)methyl or 2-Methoxymethyl Groups at the Aryl Nucleus

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Summary Introduction of 2-(dimethylamino)methyl or 2-methoxymethyl groups at the aryl nucleus of phenylcopper enhances the thermal, oxidative, and hydrolytic stability of the copper-carbon bond.

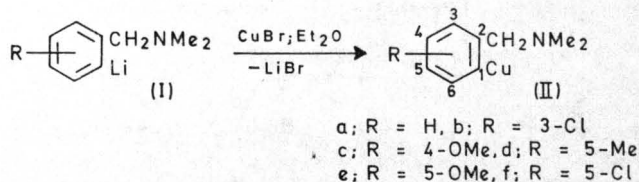
WE report on the synthesis of a variety of substituted arylcoppers, the greater part of which are thermally stable up to 100–200° and unlike the recently reported perhalogenated arylcoppers¹ are only slowly attacked by water and oxygen.

Our results show that considerable stabilization (both thermal, oxidative, and hydrolytic) of the Cu–C bond in aryl-Cu^I compounds may be brought about by the introduction of appropriate electron-donating substituents in specific positions of the aryl nucleus. Substituents containing a heteroatom, such as (dimethylamino)methyl or methoxymethyl are particularly effective† probably as a result of intra- or inter-molecular Cu–N or Cu–O coordinative bonding. This stabilizing effect is surprising

† Other stabilizing groups are methoxy, dimethylamino, diphenylphosphino, or dimethylsulphamoyl groups (see ref. 2).

since *external* ligands containing similar electron-donating heteroatoms, *e.g.* pyridine or triphenylphosphine, do not stabilize the Cu–C bond in phenylcopper.³

Arylcopper compounds containing a 2-(dimethylamino)methyl group have been obtained (40–60%, after recrystallization from ether, benzene, or benzene-pentane mixture) from the reaction of the corresponding organolithium compounds⁴ with cuprous bromide:



The identity of these organocoppers has been established by elemental analysis, i.r. and n.m.r. spectroscopy as well as

by degradation with D₂O (which for some of the compounds required forced conditions).

The decomposition temperatures of the compounds (IIa)—(IIf), which were determined by heating the solids in capillary tubes in a nitrogen atmosphere, depend on the type and site of attachment of the groups R at the phenyl nucleus. For example, (IIa) (tetrameric in benzene), (IIc) and (IIe) decompose in the range of 170—205°, whereas (IIb), (IIc), and (IIf) decompose at temperatures between 120 and 145°. The compounds (IIc)—(IIf) are very stable against air and moisture; (IIf) remains unchanged upon exposure to the atmosphere for 24 h.

In a similar way as described above 2-cuprio-1,3-bis-[(dimethylamino)methyl]benzene (30% yield, decomp. >130°) and 1-methoxy-4-[(dimethylamino)methyl]-5-cuprionaphthalene (42% yield, decomp. 162—165°, very stable against water) were obtained.

As examples of methoxymethyl-substituted phenylcoppers, 2-cuprio(methoxymethyl)benzene (*via* the Grignard route; isolated as the complex RCu·MgBr₂ in 22%

yield; decomp. >110°) and 2-cuprio-1,3-bis(methoxymethyl)benzene (25%; decomp. 170—174°) were prepared.

The organocoppers described above form complexes with well-defined stoichiometries with a variety of metal salts, † *e.g.* (IIa) yields RCu·CuBr (IIg; 78%), RCu·SnBr₂ (IIh; 90%) and RCu·2MgBr₂ (IIi; 60%).

The structure of the complexes (IIa—i) is currently being investigated.

The organocoppers as well as their complexes with metal salts are useful as intermediates in organic synthesis. For example, the reaction of (IIa) with 4-nitrobenzoyl chloride and with allyl bromide afforded 2-[(dimethylamino)methyl]-4'-nitrobenzophenone (75% yield) and 2-[(dimethylamino)methyl]allylbenzene (95% yield), respectively.

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† Complex formation of this type probably interfered with earlier attempts to isolate pure phenylcopper *via* the Grignard route.⁵

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