Novel Aryl-bridged Tetranuclear Copper–Lithium Cluster Compounds: Synthesis and Characterization by ^{13}C and ^{1}H Nuclear Magnetic Resonance Spectroscopy of Bis-{2-[(dimethylamino)methyl]phenyl}copper(I) Lithium

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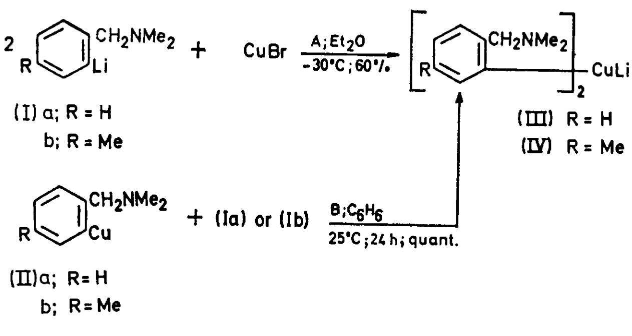
Summary The synthesis of two dimeric bis(substituted-aryl)copper(I) lithium compounds is described; ^{1}H and ^{13}C n.m.r. spectroscopy reveal a structure consisting of a Cu_2Li_2 cluster with aryl groups bridging a copper and a lithium atom.

Little is known definitely about the structure of the organocuprates.[1–4]

We report here the synthesis of thermostable bis(aryl)-copper(I) lithium compounds and the assignment of their structure as tetranuclear mixed Cu–Li cluster compounds with bridging aryl groups.



Compounds (III) and (IV) have been prepared *via* routes A and B.† The colourless compounds‡ (III) and (IV) (decomp. 178—192 °C), which are soluble in both ether and hydrocarbon solvents, exist in benzene as discrete dimeric units $R_4Cu_2Li_2$ (by cryoscopy and by ebullioscopy).

The arrangement of the aryl groups around the Cu_2Li_2 units in (III) and (IV) follows from their ^1H and natural abundance ^{13}C n.m.r. spectra. The ^{13}C resonances (relative to Me_4Si, with proton decoupling) at the lowest field [in C_6D_6: (IIa), 157·11(s); for (III), 168·10 p.p.m. (q)]§ have been assigned to C-1, which is directly bound to the metal cluster, *i.e.* in the case of (IIa) the C-1 atom bridging two Cu atoms.¶ In the ^{13}C n.m.r. spectra of (III) and (IV) these resonances appear as quartets [for (III): J 7·1 Hz] as a result of ^{13}C–^7Li coupling of the C-1 atom with only *one* Li atom. The ^1H n.m.r. spectrum of (III) displays only one quartet [(III) in [$^2H_8$]toluene: 8·74 p.p.m.; $J_{5,6}$ 7; $J_{4,6}$ 1·5 Hz] for the *ortho* protons H-6 in the four aryl nuclei [(IV) displays one doublet]. This, together with the ^{13}C n.m.r. results points out that all four 2-[(dimethylamino)methyl]phenyl groups are bound in the same manner to the metal cluster system; *i.e.* each aryl group bridges a Li and a Cu atom.** The NMe and NCH_2 proton resonance pattern [temp. dependent, for (III); NMe −60° 1·90 (s) and 1·22 (s), collapse at 5° to a singlet, 25° 1·74 p.p.m.; NCH_2, 25° 4·12 (d) and 2·48 (d), J_{gem} 11·6 Hz, collapse at 80° to a singlet, 110° 3·36 p.p.m. (br)] indicate that: (i) the four "hard" CH_2NMe_2 ligands are co-ordinated to the same metal atom, *i.e.* to lithium in view of the HSAB principle;[8] (ii) an exchange process $NMe_{2coord} \rightleftarrows NMe_{2free}$ occurs.

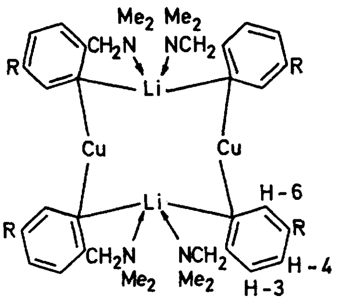


FIGURE. (III), R = H-5; (IV), R = Me

The combined data are consistent with the structure presented in the Figure.

Our results indicate that organocuprates (*e.g.* R_2CuLi, R_2CuMgX,[4] $R_6Cu_4Mg{\cdot}Et_2O$[9]) are in fact metal-Cu cluster compounds with bridging R groups.†† The consequences of such a structure with respect to their reactivity in cross coupling and conjugate addition reactions are obvious; *e.g.* the increasing reactivity of organocopper lithium compounds when the carbon ligands are $N{\equiv}C^-$,[11] $RC{\equiv}C^-$,[11] Ar^-, and Alk^- parallels the decreasing bridging ability[12] of these groups; the metal-halogen exchange[3] as a side-reaction in cross coupling reactions of aryl iodides with $(Me_2CuLi)_n$ can be explained by a nucleophilic attack of the bridged Me group on the I atom of ArI affording MeI and the more stable phenyl-bridged CuLi cluster.

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† Since both the organo-lithium(I)[5] and copper(II)[6,7] compounds occur as tetranuclear clusters the synthesis of (III) and (IV) *via* route B can be envisaged as an interaggregate exchange between two tetranuclear clusters.

‡ Correct Cu analysis were found; C, H, and N analyses were hampered by the extreme air sensitivity of these compounds.

§ Complete ^{13}C n.m.r. data will be published in the full paper.

¶ *X*-Ray diffraction analysis has established the presence of bridging aryl groups in (IIa), see ref. 7.

** In the analogous bis-{2-[(dimethylamino)methyl]phenyl}silver(I) lithium dimer the C-1 atom couples with both one Li and one Ag atom; A. J. Leusink, J. W. Marsman, G. van Koten, and J. G. Noltes, to be published.

†† Mol. wt. determinations have revealed $[2\text{-}Me_2NC_6H_4Cu]_2{\cdot}CuBr$[10] and its AgBr[10] analogue to be hexanuclear ($R_4Cu_6Br_2$ and $R_4Cu_4Ag_2Br_2$). *X*-Ray diffraction analysis has established a Cu_6 cluster structure with bridging Br and R groups for the CuBr complex, J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, in preparation.

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