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Preliminary communication

STABLE TETRANUCLEAR 4-TOLYL-COPPERLITHIUM ("CUPRATE")
 AND -GOLDLITHIUM ("AURATE") COMPOUNDS

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Summary

Di-4-tolyl-copperlithium and -goldlithium monocetherate are stable tetranuclear species, with $4\text{-Tol}_4\text{M}_2\text{Li}_2 \cdot 2\text{Et}_2\text{O}$ stoichiometry, in which the four 4-tolyl groups each bridge one Group IB metal and one lithium atom while each lithium atom further coordinates with one ether molecule.

In previous papers we showed that a variety of aryl-Group IB metal compounds, in which the aryl group bears a built-in ligand, have as a characteristic structural feature the presence of a homo- or hetero-nuclear metal core to which the aryl groups are bound via $2e-3c$ carbon-to-metal bonds with additional metal-ligand coordination taking place. Examples are R_4Cu_4 [1], $\text{R}_4\text{M}_2\text{Li}_2$ ($\text{M} = \text{Cu}, \text{Ag}$ or Au) [2] or $\text{R}_4\text{Cu}_2\text{Au}_2$ [2] in which $\text{R} = 2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$ and $\text{R}'_4\text{Cu}_4\text{X}_2$ ($\text{X} = \text{Br}$ [3] or $\text{C}\equiv\text{CR}''$ [4]) or $\text{R}'_4\text{M}_4\text{Au}_2\text{X}_2$ ($\text{M} = \text{Cu}$ or Ag) [3,5] in which $\text{R}' = 2\text{-Me}_2\text{NC}_6\text{H}_4$. Polynuclear structures are also found when intramolecular ligands are absent, e.g. $(\text{C}_6\text{F}_5)_4\text{Cu}_4$ [6], $(2\text{-CF}_3\text{C}_6\text{H}_4)_4\text{Cu}_4$ [6]*, $\text{Tol}_6\text{Au}_2\text{Zn}_2$ [7] and $\text{Tol}_6\text{Cu}_4\text{Mg}\cdot\text{Et}_2\text{O}$ [8].

We have reexamined earlier reported 2- and 4-tolylcopper [10a] and have found that also these simple arylcopper compounds exist in benzene as tetranuclear species Tol_4Cu_4 [5,9]. This was shown by molecular weight determinations and by the selective formation of 4,4'-bitolyl in the catalytic decomposition of 4-tolylcopper with CuOTf^{**} and the selective formation of 2,2'-bitolyl upon thermolysis of a benzene solution of 2-tolylcopper [9]. Both reactions involve pairwise release of tolyl groups from the tetranuclear copper

*F—Cu interaction cannot be excluded.

**OTF = trifluoromethanesulphonate (triflate).

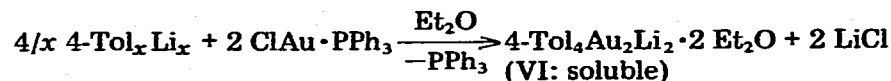
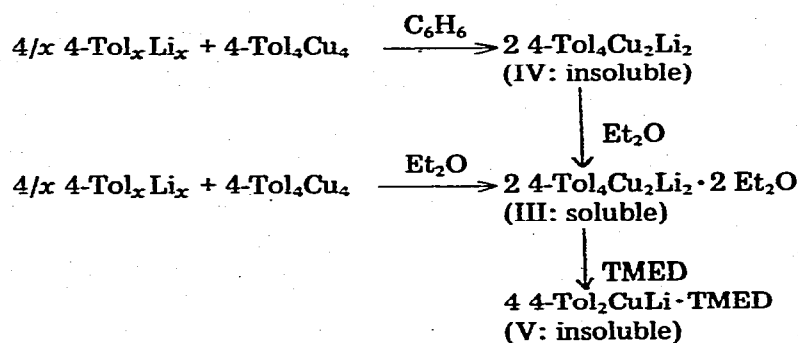
aggregate (in which tolyl groups each bridge two Cu atoms) via a non-free radical pathway [5,9]. Contrary to the proposal by Camus [10b], it seems likely that these compounds also exist as discrete polynuclear molecular units (2-Tol₆Cu₆ and 4-Tol₄Cu₄, respectively cf. ref. 9) in the solid state.

These findings confirm that the presence of an intramolecular ligand in ArCu is not a prerequisite for the formation of polynuclear Group IB metal structures*.

We report here tolyl-copperlithium and -goldlithium compounds as examples of thermally stable "cuprate" and "aurate" reagents. Knowledge about the structure of these compounds can contribute to a more realistic interpretation of the reactivity of arylcuprates in organic synthesis**.

The 1/1 reaction of pure, yellow 4-Tol₄Cu₄ (I) with pure 4-TolLi (II)*** (Cu/Li = 1/1) in ether afforded a clear yellow solution from which pale-yellow di-4-tolylcopperlithium monoetherate (III) was isolated in 84% yield. When the reaction was carried out in benzene, unsolvated di-4-tolylcopperlithium (IV: 92% yield) precipitated quantitatively^o. Addition of exactly one equivalent of diethyl ether to a suspension of IV in benzene gave a solution of III. In contrast, slow addition of TMED^{oo} to a solution of III in benzene results in precipitation of insoluble Tol₂CuLi·TMED (V) which is completed when a 1/2 Tol₄Cu₂Li₂·2 Et₂O/TMED molar ratio is reached.

Molecular weight determinations of III in benzene revealed a tetranuclear structure 4-Tol₄Cu₂Li₂·2 Et₂O [Cryoscopy found (calcd.) 630 (653)].



By a route analogous to that used for the synthesis of R₄Au₂Li₂ (R = 2-Me₂NCH₂C₆H₄ [2], 2-Me₂NC₆H₄ [5] or 2,6-(MeO)₂C₆H₃ [2]), 4-Tol₄Au₂Li₂·2Et₂O VI was synthesized. Thus the 1/2 reaction of AuCl·PPh₃ with II yielded

*In this connection the polynuclear nature of the alkyl-Group IB metal compounds (Me₃SiCH₂)₄Cu₄ (full details are in ref. 11) and Me₄Cu₂Li₂ [12] is of interest.

**For a review see ref. 13.

***In benzene 4-TolLi most probably exists as a polynuclear species: cf. 5-Me-2-Me₂NCH₂C₆H₄Li has a tetrameric structure in benzene containing bridging aryl groups [2a].

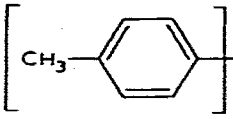
^oSimilarly, di-2-tolylcopperlithium was prepared.

^{oo}TMED = N,N'-tetramethylethylenediamine.

a solution of the aurate in ether from which VI was isolated in 90% yield. Like the cuprate compound III, VI is soluble in both ether and benzene. III decomposes at 135°C and unsolvated 4-Tol₄Cu₂Li₂ decomposes at slightly lower temperatures (±110°C), whereas the AuLi compound VI is only stable up to 60°C*. All three compounds are extremely sensitive towards oxygen and moisture.

NMR data for III and VI are given in Table 1, and the NMR spectrum of III is shown in Fig. 1. Only one resonance pattern is observed for the four 4-tolyl groups which points to a *trans* metal structure for the M₂Li₂ core. More-

TABLE 1
¹H NMR DATA FOR THE COMPOUNDS III AND VI

 $\left[\text{CH}_3\text{-C}_6\text{H}_4 \right]_4 \text{M}_2\text{Li}_2 \cdot 2 \text{Et}_2\text{O}$	δ (ppm) ^a				
	H(2)	H(3)	4-CH ₃	OCH ₂	CH ₃
III, M = Cu	8.20(d) <i>J</i> _{2,3} 7.5 Hz	7.0(d)	2.08(s)	2.72(q)	0.64(t)
VI, M = Au	7.85(d) <i>J</i> _{2,3} 7.5 Hz	7.05(d)	2.15(s)	2.85(q)	0.75(t)

^aIn benzene-d₆; TMS internal standard.

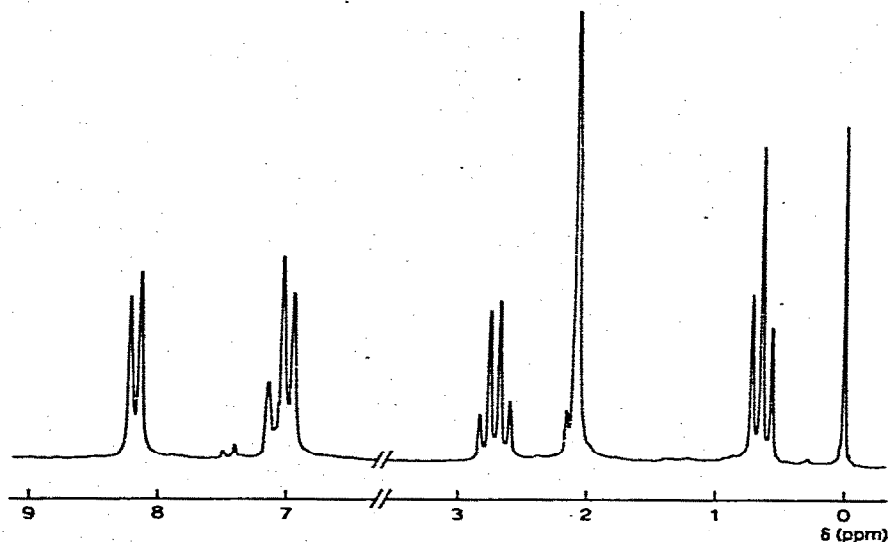


Fig. 1. 90 MHz ¹H NMR spectrum of 4-Tol₄Cu₂Li₂ · 2 Et₂O in benzene-d₆.

*For a discussion of the relation between the mode of bonding and the kinetic stability of aryl-Group IB metal compounds, see refs. 5 and 9.

over, the spectra confirm that other tetranuclear species (e.g. $4\text{-Tol}_4\text{M}_4\text{-}_n\text{Li}_n$, $n = 0, 1, 3, 4$) are absent. The high field shifts of the CH_2 and CH_3 resonances (likewise observed in $4\text{-Tol}_6\text{Cu}_4\text{Mg}\cdot\text{Et}_2\text{O}$ [8]) point to coordinated Et_2O , while the observation of only one pattern for these protons indicates that coordination with either the Group IB metal M or with lithium occurs. Furthermore, the peak area ratios confirm the $2/4 \text{ Et}_2\text{O}/\text{Tol}$ ratio in both III and VI.

On the basis of these data and by analogy with the structures of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{M}_2\text{Li}_2$ ($\text{M} = \text{Cu}, \text{Ag}$ or Au) [2], the structure in Fig. 2 is proposed for III and VI. In this structure the Group IB metals each have digonal coordination symmetry while the lithium atoms are three coordinate.

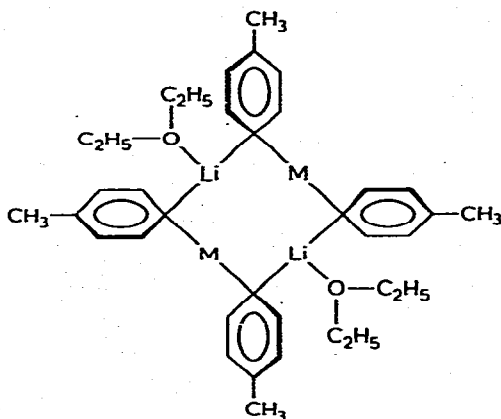


Fig. 2. Structure proposed for the $4\text{-Tol}_4\text{M}_2\text{Li}_2\cdot 2 \text{ Et}_2\text{O}$ compounds III ($\text{M} = \text{Cu}$) and VI ($\text{M} = \text{Au}$).

This coordination symmetry for Li was also found in tetranuclear $(o\text{-FC}_6\text{H}_4)_4\text{Li}_4\cdot 4 \text{ OEt}_2$ [14]. The tolyl groups each bridge one Group IB metal and one lithium atom via a $2e-3c$ carbon-to-metal interaction. It is noteworthy that the *ortho*-protons in the 4-tolyl groups of III and of $4\text{-Tol}_6\text{Cu}_4\text{Mg}\cdot\text{Et}_2\text{O}$ [8] are both observed at low field (8.20 and 8.18 ppm, respectively).

For $4\text{-Tol}_2\text{CuLi}\cdot\text{TMED}$ the ion-pair structure $4\text{-Tol}_2\text{Cu}^-\text{Li}^+\text{TMED}$ may be considered; this would involve redistribution of electron density in the $4\text{-Tol}_4\text{Cu}_2\text{Li}_2$ aggregate resulting from a shift of $2e-3c$ to $2e-2c$ metal-to-carbon bonding with concomitant stabilization of the Li^+ cation by complex formation with TMED. In this respect the bonding situation may be comparable to that proposed for the recently reported $\text{Ph}_3\text{AuZn}\cdot\text{TMED}$ [7]. Similar shifts from $2e-3c$ to $2e-2c$ metal-to-carbon bonding were observed in $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Au}_2\text{Cu}_4\text{X}_2$ ($\text{R}_2\text{Au}^-\text{Cu}_4\text{X}_2^{2+}\text{-AuR}_2$) [5].

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