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GROUP IB ORGANOMETALLIC CHEMISTRY

XXIX *. SYNTHETIC AND STRUCTURAL ASPECTS OF POLYNUCLEAR ARYLCOPPERLITHIUM COMPOUNDS $Ar_4Cu_2Li_2$ ("ARYLCUPRATES") AND INTERAGGREGATE EXCHANGE PHENOMENA IN $Ar_4Cu_4/Ar_4Li_4/Ar_4Cu_2Li_2$ SYSTEMS

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Summary

The thermally stable arylmetal-IB-lithium compounds $(2\text{-}Me_2NCHZC_6H_4)_4M_2Li_2$ (M = Cu, Ag or Au; Z = H or Me) and $(2\text{-}Me_2NC_6H_4)_4M_2Li_2$ have been prepared by a 2/1 molar reaction of the aryllithium compounds with the corresponding metal-IB halide (Cu or Ag) or metal-IB halide phosphine complex ($BrAuPPh_3$). These tetranuclear complexes were also made by an interaggregate exchange reaction of the pure arylmetal-IB clusters with the aryllithium compound.

The structure of these compounds in solution consists of aryl groups bridging one metal-IB and one lithium atom of a *trans* M_2Li_2 core. The four built-in ligands coordinate to lithium resulting in two-coordination at M and four-coordination at Li. These conclusions were based on ^1H and ^{13}C NMR spectroscopic data ($J(Ag—C(1))$, $J(Li—C(1))$) of solutions of these tetranuclear compounds as well as on the ^{197}Au Mössbauer data of solid $(2\text{-}Me_2NC_6H_4)_4Au_2Li_2$ (IS 5.65 mm/s and QS 12.01 mm/s).

The interaggregate exchange between the tetranuclear species is discussed in terms of an associative mechanism involving formation of an octanuclear intermediate in which the aryl groups can migrate via (3*c*—2*e*)edge—(2*c*—2*e*)corner—(3*c*—2*e*)edge movements without M_2—Ar bond cleavage.

Some aspects of the organic reactions in which organocuprates are involved as intermediates are discussed in terms of the novel structural information.

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* For Part XXVIII see ref. 1.

TABLE 1

ORGANOCUPRATE SPECIES WHICH HAVE BEEN STRUCTURALLY CHARACTERIZED TO SOME EXTENT

Compound	Ref.	Proposed structure	Studied by	Stable at (°C)
MeCu/MeLi	6–9	$Me_4Cu_2Li_2$ [a, b]	^1H NMR; X-ray [9]; mol. wt.	<0
BuCu/BuLi/LiX/phosphines	10	Polynuclear structures [b, c]	^1H NMR; mol. wt.	<0
$Me_3SiCH_2Cu/Me_3SiCH_2Li$	11, 12	$(Me_3SiCH_2)_4Cu_2Li_2$ [a, b]	^1H NMR; mol. wt.	Room temperature
$PhCu \cdot PhLi \cdot n\ Et_2O$; $(PhCu)_4 \cdot PhLi \cdot 3.5\ Et_2O$; $(PhCu)_2Ph_2Mg \cdot n$ THF	13	d	Isolated [e]	Room temperature
m-TolCu/m-TolLi	14	d	Isolated [e]	Room temperature
p-TolCu/p-TolLi	15	p-$Tol_4Cu_2Li_2 \cdot 2\ Et_2O$	Isolated [e]; ^1H and ^{13}C NMR; mol. wt.	Room temperature
$Ph_2Mg \cdot 4\ PhCu \cdot Et_2O$	16	$Ph_6MgCu_4 \cdot Et_2O$	Isolated [e]	Room temperature
p-$Tol_2Mg \cdot 4$ p-$TolCu \cdot$ solv.		p-$Tol_6MgCu_4 \cdot$ solv.	^1H NMR; mol. wt.	
5-R-2-$Me_2NCH_2C_6H_4Cu$/5-R-2-$Me_2NCH_2C_6H_4Li$ R = H or R = Me	4 [f]	$Ar_4Cu_2Li_2$	Isolated [e]; ^1H and ^{13}C NMR; mol. wt.	110
2-$Ph_2PCH_2C_6H_4Cu$/2-$Ph_2PCH_2C_6H_4Li$	17	$R_2CuLi \cdot LiBr \cdot Et_2O$ [d]	Isolated [e]	Room temperature

[a] The tetranuclear structure proposed by the authors in refs. 6–8 has been based on the ^{13}C and ^1H NMR results presented for $(2\text{-}Me_2NCH_2C_6H_4)_4\text{-}Cu_2Li_2$ [4] and $\text{-}Ag_2Li_2$ [5] (cf. Fig. 1 of this paper). [b] Structural investigations carried out on solutions of the compounds prepared in situ. [c] Various types of polynuclear structures were deduced from ^1H NMR *and colligative studies.* [d] *Not specified by the authors.* [e] Stoichiometry indicated based on *elemental analytical* data. [f] And this paper.

Introduction

Previous studies have shown that organocuprates are powerful reagents for the synthesis of a wide variety of otherwise not easily accessible organic compounds. The synthetic applications of these reagents have recently been reviewed by Normant [2a] and Posner [2b]. Despite the enormous amount of information on the reactivity of the organocuprates, mechanistic discussions have remained largely speculative because of the limited knowledge about the reactive species [3].

The compounds which have so far been isolated and of which the structures have been studied by physico-chemical techniques are listed in Table 1. Recently, Pearson and Gregory [9] proposed, on the basis of extensive spectroscopic data, a tetranuclear structure $Me_4Cu_2Li_2$ for the well-known MeCu/MeLi reagent in ether solution. Later, Ashby [8] and San Filippo [10] independently reported spectroscopic studies on various types of alkylcopperlithium species prepared in situ. In 1972 we reported on the isolation and structural characterization of an ArCu/ArLi reagent with Ar = $2\text{-}Me_2NCH_2C_6H_4$ and showed for the first time that this type of cuprate species has a tetranuclear structure, $Ar_4Cu_2Li_2$, containing *3c—2e* bonded aryl groups each bridging one copper and one lithium atom [4].

In the course of our later studies on the structure—reactivity relationship of arylmetal-IB clusters it appeared that $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ was representative of a larger group of compounds having $Ar_4\,M_2Li_2$ stoichiometry. For example, in the case of $Ar_4Ag_2Li_2$, the tetranuclear structure was unambiguously established by ^{13}C NMR investigations [5]. The tetranuclear structure with bridging aryl groups appears to be an intrinsic feature of the metal-IB-lithium clusters and is independent of the presence of built-in ligands. This is exemplified by the structure of the simple aryl-copperlithium and -goldlithium compounds $(p\text{-tolyl})_4M_2Li_2 \cdot 2\,OEt_2$ [15].

In this paper we report the results of a study of the synthesis and identification of $2\text{-}Me_2NCH(Z)$— (Z = H or Me) substituted arylcopperlithium compounds, and also of *p*-tolylcopperlithium, which is a representative of cuprates lacking built-in ligands.

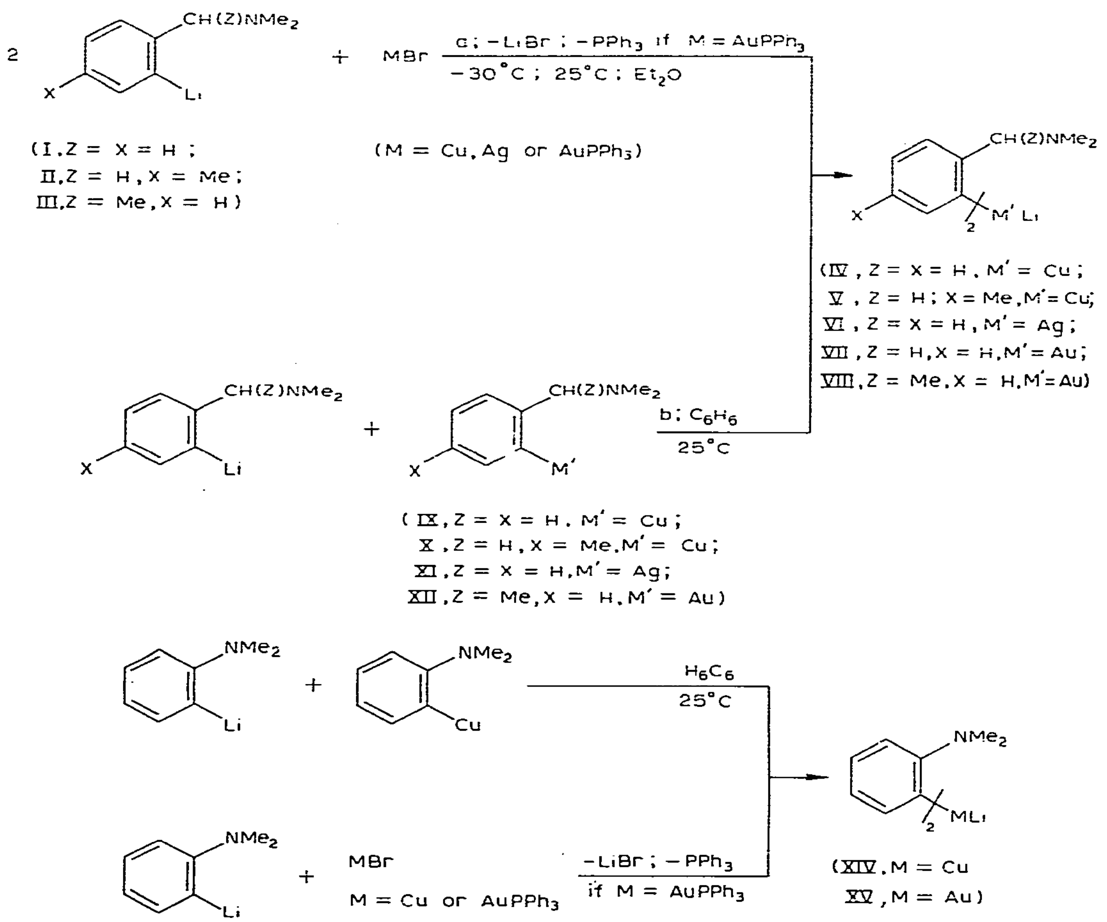
Appropriate synthetic and spectroscopic aspects of the corresponding silver and gold derivatives will also be included. Moreover, the reactivity of these compounds towards Lewis bases, as well as some of the implications of the structural data for the reactivity of the cuprate compounds in organic synthesis, will be discussed.

Results and discussion

Synthesis of $[2\text{-}Me_2NCH(Z)C_6H_4]_2MLi$ (Z = H or Me) and $(2\text{-}Me_2NC_6H_4)_2MLi$ (M = Cu or Au)

Two general routes are available for the preparation of arylmetal-IB-lithium compounds (cf. Scheme 1). Reaction (a) involves the 1/2 reaction of the metal-IB salts with either 2-[(dimethylamino)methyl]phenyllithium (I) or the C-chiral aryllithium compound [18] 2-{1-[(*S*) or (*R*)]-(dimethylamino)ethyl} phenyllithium (III). For reasons discussed earlier (see ref. 19) it is important that the

SCHEME 1. Synthesis of arylmetal-IB-lithium compounds



metal halide is added to the organolithium reagent. In this way, 2-[(dimethylamino)methyl]phenylcopperlithium (IV) was prepared in about 50% yield. The copper analysis of the white product (found: Cu, 18.8; calcd.: Cu, 18.68%) as well as ^{1}H NMR (vide infra) and IR spectroscopy (*ortho*-disubstitution pattern for the aryl nucleus [20]) pointed to the isolation of pure IV.

The attempted synthesis of the 5-methyl-substituted derivative (V) via route (a) initially afforded a product which, according to the copper analysis (found: Cu, 20.1; Ar_2CuLi calcd.: Cu, 17.32; 2 $Ar_2CuLi \cdot ArCu$ calcd.: Cu, 20.08%) and NMR spectroscopy [peak area ratio $NCH_2(Ar_2CuLi)/NCH_2(ArCu) \approx$ 1.8/1 (calcd. from Cu analysis 2/1)] had the composition $Ar_5Cu_3Li_2$ (Ar = 5-Me-2-$Me_2NCH_2C_6H_3$) *. Addition of one equivalent of the organolithium compound II to a solution of this product in benzene afforded a white solid V which was found by NMR spectroscopy (absence of the starting product II

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* NMR spectroscopy revealed that in solution various polynuclear species are present (cf. Fig. 3).

as well as of the organocopper X) to be pure Ar_2CuLi.

The corresponding organosilverlithium compound VI was similarly prepared by route (a) (cf. ref. 5). The arylgoldlithium compounds VII * and VIII [18] were synthesized by the reaction of bromo(triphenylphosphino)gold(I) with 2-[(dimethylamino)methyl]phenyllithium I or the C-chiral compound III. In these reactions, which were carried out in ether at 0°C, the arylgoldlithium compounds precipitated out. Triphenylphosphine and LiBr were isolated quantitatively from the solution.

The arylmetal-IB-lithium compounds IV—VIII were also prepared by the 1/1 molar reactions of the respective arylmetal-IB compounds IX—XII with the corresponding organolithium compounds in benzene as solvent (route b, Scheme 1). The preparation (vide infra) and the structural characterization of the arylmetal-IB compounds IX—XII are described elsewhere [22,23].

The 2-dimethylamino-substituted diphenyl-copperlithium (XIV) and -goldlithium (XV) compounds were prepared by the same routes [24].

The arylmetal-IB lithium compounds IV—VIII, XIV and XV appeared to be extremely reactive towards oxygen and water. Upon exposure to the atmosphere, rapid decomposition occurred. The solid compounds IV—VIII, XVI and XV decomposed upon heating in a capillary tube (under N_2; heating rate 5°C/min) between 140 and 200°C. This implies a surprisingly high thermostability for this type of compound (cf. data in Table 1). Solutions in toluene or benzene can be heated at 80°C for several hours without observable decomposition. Moreover, a solution of IV in benzene showed an unchanged NMR spectrum after storage for 4 years at ambient temperatures. However, these solutions are very sensitive towards traces of water; hydrolysis gives rise to the formation of the arylmetal-IB compound (ArM) and the arene (ArH), both being detectable by NMR spectroscopy.

$$Ar_2MLi \xrightarrow{x\ H_2O} (1-x)Ar_2MLi + x\ ArM + x\ LiOH + x\ ArH$$

Structural characterization of the compounds IV—VIII, XIV and XV

The degree of association of the compounds was determined by cryometry as well as by ebulliometry (see Table 2). Before and after each measurement the NMR spectrum of the solution was recorded to ascertain that decomposition had not occurred. The data in Table 2 indicate that both the $2\text{-}Me_2NCH_2$- and the $2\text{-}Me_2N$-substituted metal-IB-lithium compounds exist in both boiling and freezing benzene as discrete dimeric species with $Ar_4M_2Li_2$ stoichiometry.

The structure of the $Ar_4M_2Li_2$ compounds in benzene solution has been studied by ^{13}C and ^{1}H NMR spectroscopy (see Tables 3 and 4). In this paper the overall structural features will be discussed, while the dynamic stereochemistry and the bonding in these clusters will be described later [23].

Some of the observed ^{13}C chemical shift data and assignments have been compiled in Table 3. For comparison, ^{13}C NMR data for three other compounds having Ar_4M_4 stoichiometry are included, viz. the organocopper compounds $(2\text{-}Me_2NCHZC_6H_4)_4Cu_4$ (IX, Z = H [4,20] and (*S*)-X, Z = Me [18]) and the

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* Preliminary data for this compound were reported in ref. 21.

TABLE 2

MOLECULAR WEIGHTS AND DECOMPOSITION POINTS OF THE Ar_2MLi COMPOUNDS

Compound Ar_2MLi		Dec. (°C)	Mol. wt., found [a] (calcd.) [b]	Degree of association $\bar{n}$
Ar	M			
IV, 2-$Me_2NCH_2C_6H_4$ [c]	Cu	178—182	C 711 (338.5)	2.1
			E 635	1.9
V, 5-Me-2-$Me_2NCH_2C_6H_3$	Cu	157—192	C 722 (366.5)	2.0
VI, 2-$Me_2NCH_2C_6H_4$ [d]	Ag	180	C 812 (383.2)	2.1
			E 723	1.9
VII, 2-$Me_2NCH_2C_6H_4$	Au	202 [e]	E 931 (472.3)	2.0
VIII, 2-$Me_2NCH(Me)C_6H_4$ [f]	Au	140	C 950 (500)	1.9
XIV, 2-$Me_2NC_6H_4$	Cu	133—137		
XV, 2-$Me_2NC_6H_4$	Au	155—160 [g]	E 920 (444)	2.1

[a] Mean values are given (in benzene; concentration range 1×10^{-2}—5×10^{-2} *M*; C by cryometry, E by ebullioscopy; concentration independent). [b] Calcd. for Ar_2MLi. [c] Mol. wt. (cryometric in benzene) of IV/PPh_3 mixtures; mol. ratio Ar_2CuLi/PPh_3 1/2, calcd. if no complex formation occurs $n = 3.0$, found $n = 3.1$; mol. ratio 1/4, calcd. $n = 5.0$, found $n = 5.2$. [d] See ref. 5. [e] Slow at 170°C. [f] Configuration at C is (*S*). [g] Heating in air; explosion at 175°C.

organolithium compound $(5\text{-Me-2-}Me_2NCH_2C_6H_3)_4Li_4$ (II) [4] (vide infra).

As is evident from Table 3, the low-intensity resonance at lowest field has been assigned to the carbon atom C(1) which is bound to the metal system, i.e. in the case of $(5\text{-Me-2-}Me_2NCH_2C_6H_3)_4Cu_4$ (X) to the bridging carbon atom *. For the elucidation of the structures of the $Ar_4M_2Li_2$ compounds it is important that in the spectra of $Ar_4Cu_2Li_2$ (IV) and $Ar_4Au_2Li_2$ the resonance for C(1) appears as a quartet ($J \approx 7$ Hz). The observed multiplicity, which has been ascribed to ^{13}C—^{7}Li coupling, reveals that each phenyl group is bonded to one lithium atom only. The structure shown in Fig. 1 in which each aryl group bridges one copper and one lithium atom via C(1) fully accounts for these data.

The presence of aryl groups bridging one lithium and one silver atom in the corresponding silverlithium compound $Ar_4Ag_2Li_2$ (VI), has been unambiguously established by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C resonance of C(1) in $Ar_4Ag_2Li_2$ (VI) couples both with one lithium atom [$J(^{13}C—^{7}Li)$ 7.2 ± 0.2 Hz] and with one silver atom [$J(^{13}C—^{107}Ag)$ 118.3 ± 0.8 and $J(^{13}C—^{109}Ag)$ 136.0 ± 0.8 Hz] [5].

The ^{1}H NMR spectra of $Ar_4M_2Li_2$ compounds (M = Cu, Ag, Au) at room temperature show only one resonance pattern for each hydrogen (see Fig. 2 and Fig. 1 in ref. 23). E.g. the *ortho*-hydrogen atom (H(6)) appears as a sharp doublet of doublets ($J_{5,6} \approx 7$; $J_{4,6} \approx 1.5$ Hz). This indicates that all four aryl ligands are in equivalent environments, and so must be bound in the same manner to the metal system. This conclusion is unambiguously supported by the results of a full analysis of the ^{1}H NMR spectrum of $Ar_4Ag_2Li_2$ (VI), which revealed that both the aromatic and the benzylic protons coupled with one Ag nucleus only [e.g. H(6) appears as a triplet of doublets arising from one *ortho* interaction with H(5) (7.0 Hz) and one *ortho* interaction with Ag

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* For an X-ray structure see ref. 20.

TABLE 3

^{13}C NMR DATA [a] FOR SOME ARYL-METAL-IB, -METAL-IB-LITHIUM AND -LITHIUM CLUSTERS

Compound	δ (ppm)					
	NMe	NCH	5-Me	α-Me	C_2—C_6	C_1
$(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ [b]	46.6	72.4	—	—	125.3, 125.9 127.7/143.7 147.9	168.1 q J(C—Li) 7.0 Hz
−65°C [c]	42.4 and 47.7	70.7			142.1(br), 146.5 [e]	167.0 J(C—Li) 7 Hz
$(2\text{-}Me_2NCH_2C_6H_4)_4Au_2Li_2$ [d]	47.5	70.8	—	—	125.6, 127.9 128.7, 144.3, 148.2	174.4 [f]
$[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Au_2Li_2$	47.6	73.1	—	13.7		180.9 J(C—Li) ~6.0 Hz
−60°C	53.4 and 43.9	73.1	—	13.7	150.6 (br) 150.0, 158.0 [e]	180.9
$(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Cu_2Li_2$	46.6	72.0	21.7	—	125.9, 127.5, 133.9, 144.9, 145.1	[g]
$(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ [h]	49.2 (45.6)	75.3 (71.4)	—	—	128.5 (125.0), 129.0 (125.4), 129.8 (126.2), 147.3 (143.60), 156.8 (153.2)	157.1 (153.3)
$[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$ [i, j]	43.9	71.4	—	16.5	123.1, 123.2 123.9, 136.2, 150.6	157.1
$(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Li_4$ [k]	42.9 and 45.6	69.2	18.5	—	132.8 (br), 139.9, 149.1	163.9 (v br)

[a] With ^1H decoupling. Shifts relative to TMS. Ambient temperature unless otherwise stated. [b] 0.7 g of $Ar_4Cu_2Li_2$ in benzene-d_6 (4 ml). [c] In toluene-d_8. [d] 0.2 g of $Ar_4Cu_2Li_2$ in benzene-d_6 (4 ml). [e] Other resonances masked by solvent ^{13}C resonances. [f] Quartet; due to the low intensity of the multiplet accurate J values could not be determined (in the range 6—7 Hz). [g] Owing to the low solubility of V not observed. [h] 0.8 g of Ar_4Cu_4 in benzene-d_6 (4 ml). Values between parentheses: 0.2 g of Ar_4Cu_4 in pyridine-d_5 (4 ml). [i] 0.7 g of Ar_4Cu_4 in toluene-d_8. [j] For the spectra at low temperature, see ref. 23. [k] Values relative to benzene-d_6.

(H(6)—^{107}Ag −6.2; H(6) —^{109}Ag—7.1 Hz)] [5] *. Furthermore, the combined data indicate, that neither inter- nor intra-molecular exchanges are taking place on the NMR timescale.

An interesting part of the ^1H NMR spectra of these compounds is the aliphatic region, where one resonance pattern was observed for both NMe_2 and NCH_2 (and α-Me and α-H in VIII). This indicates that the built-in ligand is coordinated to only one of the two metals, i.e. to the Li or the metal-IB atoms. In the light of the HSAB principle it has been assumed that all four "hard" nitrogen ligands

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* Other compounds for which $J(^1H—Ag)$ data have been reported are: $(2\text{-}Me_2NC_6H_4)_4Ag_2Au_4Br_2$ (^3J(H(6)—Ag) 6.0 Hz) [24], $[Ph_3PCH_2AgCH_2PPh_3]Cl$ (^2J(H—Ag) 12 Hz [25a] and $[Ph_3PCH_2AgCl]_4$ (^2J(H—Ag) 14.4 Hz) [25b]. The present compound is the only one for which $J(^{13}C—Ag)$ data have been reported [5].

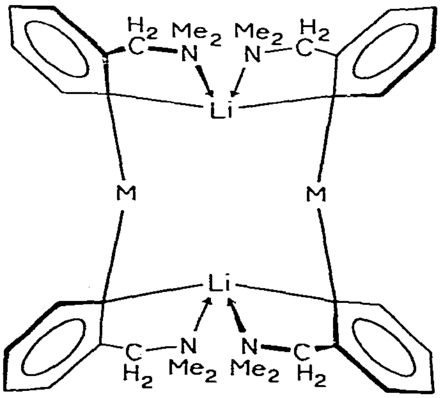

Fig. 1. Schematic structure of the $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ (M = Cu, Ag or Au) compounds. The angles at the bridging C-atoms are acute (cf. ref. 20). As a result of linear hybridization at M the C(1)MC'(1) angle formed by the interatomic vectors is smaller than 180°.

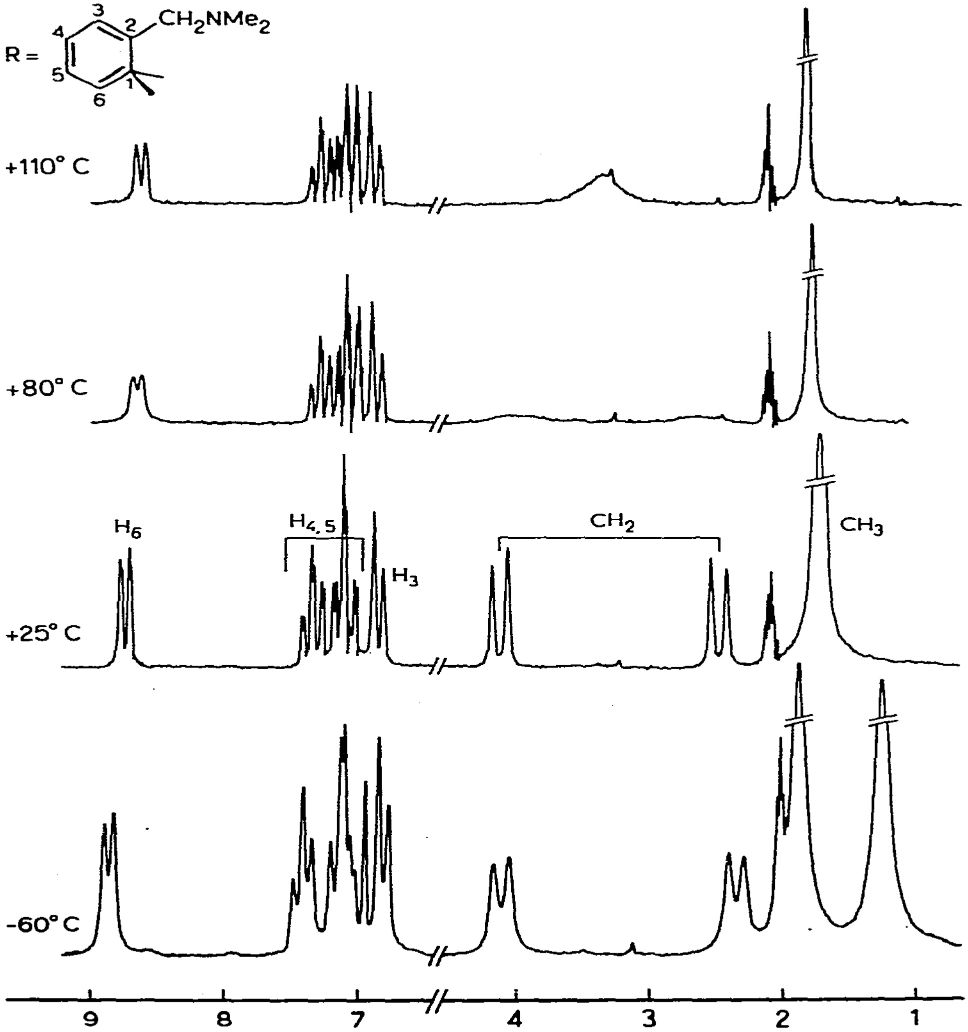

Fig. 2. ^1H NMR spectra (δ ppm) of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ in toluene-d_8 at various temperatures (see also Table 4).

TABLE 4

^{1}H NMR SPECTROSCOPIC DATA FOR SOME ARYLMETAL-IB-LITHIUM COMPOUNDS AT ROOM TEMPERATURE

Compound [a]	δ (ppm) [b]		
	NCH_3 [d]	NCH_2	H_6 [c]
$(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ (toluene-d_8)	1.74 (s)	4.12 (d) and 2.48 (d) J_{gem} 12 Hz	8.74 (m, J_{ortho} 7 J_{meta} 1.5 Hz)
$(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Cu_2Li_2$ [benzene-d_6]	1.73 (s) [e]	4.18 (d) and 2.53 (d) J_{gem} 12 Hz	8.69 (d, J_{meta} 1.5 Hz)
$(2\text{-}Me_2NCH_2C_6H_4)_4Ag_2Li_2$ [benzene-d_6]	1.74 (s)	3.96 (d) and 2.52 (d) J_{gem} 12 Hz	8.66 (m) [f]
$(2\text{-}Me_2NCH_2C_6H_4)_4Au_2Li_2$ [benzene-d_6]	1.79 (s)	4.30 and 2.41 (s) J_{gem} 12 Hz	8.42 (m)
$(S\text{-}2\text{-}Me_2NCHMeC_6H_4)_4Au_2Li_2$ [benzene-d_6]	1.75 (s)	0.88 (d, J 7 Hz) [g]; 4.84 (q)	8.62 (m)

[a] Between brackets the solvent used. [b] TMS internal. s singlet, d doublet, m multiplet, q quartet. [c] Assignment of the resonances in the low field area to the other aromatic protons is not always possible. [d] At lower temperatures this singlet decoalesces into two singlets, see ref. 23. [e] δ(5-Me) 2.52 ppm (s). [f] Chemical shift data for H(3)—H(5), see ref. 5. [g] Chemical shift data of α-CH_3 and α-H, respectively.

exclusively coordinate to the "hard" lithium atoms, which then are four-coordinate (see Fig. 1). Accordingly, the metal-IB atoms in these compounds will be two-coordinate. This is supported by the observation that the N—M interaction in Ar_4M_4 compounds, e.g. $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$, is only weak [20,23], whereas the dynamic resonance pattern of the NMe_2 protons in the $Ar_4M_2Li_2$ compounds points to an N—Li interaction which is comparable with the strong N—Li interaction in Ar_4Li_4 [23]. The fact that the metal-IB atoms are coordinatively saturated can be deduced from the following facts: (i) molecular weight determinations of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ in the presence of increasing amounts of PPh_3 reveals that complex formation with PPh_3 does not occur (see Table 2), and (ii) the PPh_3 formed in the reaction of Ar_4Li_4 with $BrAuPPh_3$ does not interfere with the isolation of pure $Ar_4Au_2Li_2$ (see Scheme 1, route b, but also the synthesis of dialkylaurates reported by Tamaki and Kochi [26]).

The proposed symmetry at the metal-IB atoms shown in Fig. 1 is based on the consideration that linear hybridization of orbitals at the metal-IB atoms (M) requires the C(1)—M—C(1) angles to be smaller than 180° [24,27]. C—Cu—C angles of 164° in $(2\text{-}Me_2NC_6H_4)_4Cu_6X_2$ (X = Br [27] and C≡C-Tol-*p* [28]) and in $(Me_3SiCH_2)_4Cu_4$ [11] have been established by X-ray diffraction.

The $(2\text{-}Me_2NC_6H_4)_2$-CuLi [24] and -AuLi compounds are likewise formulated as tetranuclear species based on molecular weight data of the goldlithium compound (see Table 2). However, for these compounds less detailed information is available. This is largely due to the limited solubility of these compounds in aromatic solvents. However, ^{1}H NMR spectroscopy reveals that the structural features of these compounds are similar to the $2\text{-}Me_2NCH_2$-substituted phenylmetal-IB-lithium compounds, i.e., a *trans*-metal arrangement in the Li_2M_2 core with 3*c*—2*e* bonded $2\text{-}Me_2NC_6H_4$ groups. That also in these compounds orbitals on Au are linearly hybridized can be deduced from the ^{197}Au Mössbauer spectrum of the $Ar_4Au_2Li_2$ compound XV. The isomer shift (IS) (5.65 mm/s) and quadrupole splitting (QS) (12.01 mm/s) are to our knowledge the largest values found so far. These IS and QS values are reasonably close to the least-squares line of a plot of QS against IS data for two-coordinate gold(I) compounds [29]. According to the 6*s*, 6*p* bonding orbital scheme for Au^I compounds [29] the high IS and QS values of XV point to extensive σ-donation by the 3*c*—2*e* bonded aryl groups in both $6p_z$ and 6*s* orbitals of Au^I. The fact that the quadrupole splitting of XV is higher (or the isomer shift lower) than expected can be due to either the presence of other metals which alter the electric-field gradient or to a contribution of π bonding effects. Further Mössbauer studies on diarylgoldlithium compounds in combination with X-ray crystal-structure determinations are needed to throw further light on this question *.

Intermolecular exchange between tetranuclear arylcopper (Ar_4Cu_4), aryllithium (Ar_4Li_4) and arylcopperlithium ($Ar_4Cu_2Li_2$) compounds

Structure of Ar_4Li_4. In order to obtain more information about the reaction leading to $Ar_4Cu_2Li_2$ compounds (Scheme 1, reaction b) it was necessary to investigate the nature of the organolithium reagents used in these reactions.

Pure 2-[(dimethylamino)methyl]phenyllithium (I) as well as its 5-methyl derivative (II) were obtained as white crystalline solids via lithium—hydrogen exchange reactions. I is highly insoluble in ethers and hydrocarbon solvents, while its 5-methyl derivative II shows excellent solubility in both types of solvents. II is extremely sensitive towards oxidation and hydrolysis, but is thermally quite stable (dec. 170—175°C).

While the structures of several alkyllithium compounds have been elucidated by X-ray crystallography (e.g. Me_4Li_4, Et_6Li_6 and c-Hx_6Li_6) (c-Hx = cyclohexyl) [31], little is known about the structure of aryllithium compounds. Molecular weight determinations have shown that *o*-FC_6H_4Li and phenyllirhium are tetrameric in THF and ether and are probably present as complexes $(RLi \cdot ether)_4$ [32], while West and Waack report phenyllithium to exist in THF as a solvated dimer [33]. Additionally, we found that simple aryl-copperlithium and -goldlithium species, where aryl = *p*-tolyl, exist in benzene as tetranuclear species with *p*-$Tol_4M_2Li_2 \cdot 2\ OEt_2$ stoichiometry [15].

Molecular weight determinations of II by cryoscopy in benzene yielded a value for *n* of 3.4 and by ebulliometry a value of $n = 4.0 \pm 0.6$. The discrepancy between these values as well as the large spread in values of *n* is ascribed to impurities formed by hydrolysis during the determination. Most probably II exists in benzene as a tetramer; we say this for two reasons **: (i) the proton NMR spectrum (which is temperature dependent, see ref. 23) showed only one resonance pattern for each of the hydrogens, and (ii) no concentration dependence is observed, and this is contrary to what would be expected if an equili-

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* Attempts to record the ^{63,65}Cu NQR spectra of the $Ar_4Cu_2Li_2$ compounds failed [30].

** Viswanathan and Wilkie [34] reported mol. wt. and ^{1}H NMR data for I in DMSO. However, the NMR data (especially the observation of only one resonance for all aromatic protons at the position of the parent arene) suggest that instead of the organolithium compound its protolysis product *N,N*-dimethylbenzylamine, originating from the reaction of I with DMSO, was being examined.

brium mixture involving aggregates with different molecular weights were present.

The ^{13}C NMR spectra (see Table 3) reveal a broad resonance for C(1). The low intensity, even at low temperature (—60°C), and the absence of specific detail does not allow a definite conclusion regarding the nature of the aryl—lithium bonding. However, the total broadness of the resonance is consistent with coupling with two lithium atoms. Although conclusive evidence regarding the structure of II is presently not available, the above findings seem to support a structure consisting of aryl groups each bridging two lithium atoms of a central Li_4 core via $3c$—$2e$ C—Li bonds analogous to the structure established for $(5\text{-Me-}2\text{-Me}_2NCH_2C_6H_3)_4Cu_4$ [20]. Moreover, in the Ar_4Li_4 structure extensive Li—N bonding occurs (cf. ref. 23).

Exchange between Ar_4Cu_4 and Ar_4Li_4. Limited information is available concerning interaggregate exchange between polynuclear organocopper species. We have presented mass spectroscopic evidence for the occurrence of interaggregate exchange between the tetranuclear compounds $2\text{-Me}_2NCH_2C_6H_4Cu$ (IX) and its 5-methyl-substituted analog [20]:

$$Ar_4Cu_4 + 5\text{-MeAr}_4Cu_4 \rightleftharpoons Ar(5\text{-MeAr})_3Cu_4 + Ar_2(5\text{-MeAr})_2Cu_4 + Ar_3(5\text{-MeAr})Cu_4$$

A similar equilibrium has been reported for the exchange between $(C_6F_5)_4Cu_4$ and $(o\text{-}CF_3C_6H_4)_4Cu_4$ *.

The tetranuclear species present in these equilibria have comparable stabilities (vide infra). Isolation of individual species from the product mixture is therefore impossible. This situation contrasts with the interaggregate exchange between p-TolC≡CCu and $2\text{-Me}_2NC_6H_4Cu$ in DMF which results in the quantitative formation (and isolation) of the hexanuclear mixed-organocopper cluster $(2\text{-Me}_2NC_6H_4)_4Cu_6(C{\equiv}CTol\text{-}p)_2$ [28].

Recently, several NMR studies have dealt with interaggregate exchange reactions of mixtures of alkyllithium and alkylcopper compounds, but specific mixed cluster species were not characterized (see Table 1). The formation of the $Ar_4Cu_2Li_2$ species in the present study from the 1/1 reaction of Ar_4Cu_4 with Ar_4Li_4 provides an other example of an exchange between two polynuclear species where the exchange product can be isolated:

$$\frac{4}{n}\,Ar_nM_n + Ar_4Li_4 \xrightarrow{C_6H_6} 2\,Ar_4M_2Li_2$$

$Ar = 2\text{-Me}_2NCH_2C_6H_4$; $M = Cu$, $n = 4$
$M = Ag$, $n = 4$ or 6
$Ar = 2\text{-Me}_2NC_6H_4$ $M = Cu$ or Au, n not defined.

As indicated in this equation, similar specific exchange reactions occur between the other arylmetal-IB and aryllithium species.

The exclusive formation of the mixed species with $Ar_4M_2Li_2$ stoichiometry, which has the metal-IB atoms and the lithium atoms arranged in a *trans* fashion (see Fig. 1), indicates that this species is more stable than either the starting polynuclear compounds or the *cis* isomer. These stability differences are a

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* Observations by Cairncross and Sheppard, cited in ref. 35.

consequence of the presence of the built-in ligand of the aryl group, since it is only in the *trans* isomer that all four 2-Me_2NCH_2 (or 2-Me_2N) ligands can coordinate with the lithium atoms *.

Exchange between Ar_4M_4 (M = Cu or Li) and $Ar_4Cu_2Li_2$

Since the 1/1 reaction between Ar_4M_4 and Ar_4Li_4 described above is complete for all combinations studied, it gives no information about the occurrence of exchange between the mixed metal compounds $Ar_4M_2Li_2$ and the starting compounds Ar_nM_n or Ar_4Li_4. The latter exchange reactions were studied for M = Cu and Ar = 2-$Me_2NCH_2C_6H_4$.

The 1/1 interaction of benzene-soluble $Ar_4Cu_2Li_2$ with benzene-insoluble Ar_4Li_4 was followed by NMR spectroscopy. No exchange takes place, because the pattern of $Ar_4Cu_2Li_2$ is exclusively observed:

$$Ar_4Li_4 + Ar_4Cu_2Li_2 \overset{C_6H_6}{\underset{25^{\circ}C}{\not\rightarrow}} 2\ Ar_4Cu_{4-n}Li_n$$

$$n = 1\text{—}3$$

The absence of exchange between Ar_4Li_4 and $Ar_4Cu_2Li_2$ accounts for the high purity in which $Ar_4Cu_2Li_2$ compounds (cf. Scheme 1) have been isolated. This is not a result of the insolubility of Ar_4Li_4 (Ar = 2-$Me_2NCH_2C_6H_4$), because benzene-soluble Ar_4Li_4 (Ar = 5-Me-2-$Me_2NCH_2C_6H_3$) likewise does not undergo exchange with $Ar_4Cu_2Li_2$ (cf. the Ar_4Cu_4/Ar_4Li_4 reaction described below).

The 2/1 reaction of benzene-soluble Ar_4Cu_4 (IX) with Ar_4Li_4 (I) afforded a clear solution. According to NMR spectroscopy both Ar_4Cu_4 and $Ar_4Cu_2Li_2$ (IV), as well as two other unknown species A and B (see Fig. 3; resonances marked with A and B) were present in solution. The area ratios of the respective CH_2-resonance patterns suggest the formation of the following equilibrium mixture:

$$\underset{(IX)}{4.50\ Ar_4Cu_4} + \underset{(I)}{2.25\ Ar_4Li_4} \xrightarrow[24\ h,\ 25^{\circ}C]{C_6H_6}$$

$$\underset{(IX)}{2.00\ Ar_4Cu_4} + \underset{(IV)}{3.00\ Ar_4Cu_2Li_2} + \underset{(A + B)}{[4\ RCu \cdot 3\ RLi]}$$

When the solution was heated to 80°C the spectrum shown in Fig. 3 was obtained. As witnessed by the sharp NCH_2, NCH_3 and H_6 proton resonances, Ar_4Cu_4 is still in slow interaggregate exchange (approximately constant NCH_3-(total)/NCH_2(Ar_4Cu_4) peak area ratio). However, the NCH_2 and NCH_3 patterns attributed to the species A and B as well as to $Ar_4Cu_2Li_2$ have collapsed to broadened singlets. Collapse of the diastereotopic CH_2 proton resonances in pure $Ar_4Cu_2Li_2$ occurs above 80°C (cf. Fig. 2) as a result of rotation of the aryl

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* The same arrangement has been found for tetranuclear *p*-$Tol_4M_2Li_2 \cdot 2\ OEt_2$. In these compounds the lithium atoms become three-coordinate by coordination with ether. The 1/1 reaction of *p*-TolM with *p*-TolLi in a non-coordinating solvent like benzene generates insoluble *p*-$Tol_4M_2Li_2$ which can be converted into soluble *p*-$Tol_4M_2Li_2 \cdot 2\ OEt_2$ by addition of Et_2O [15].

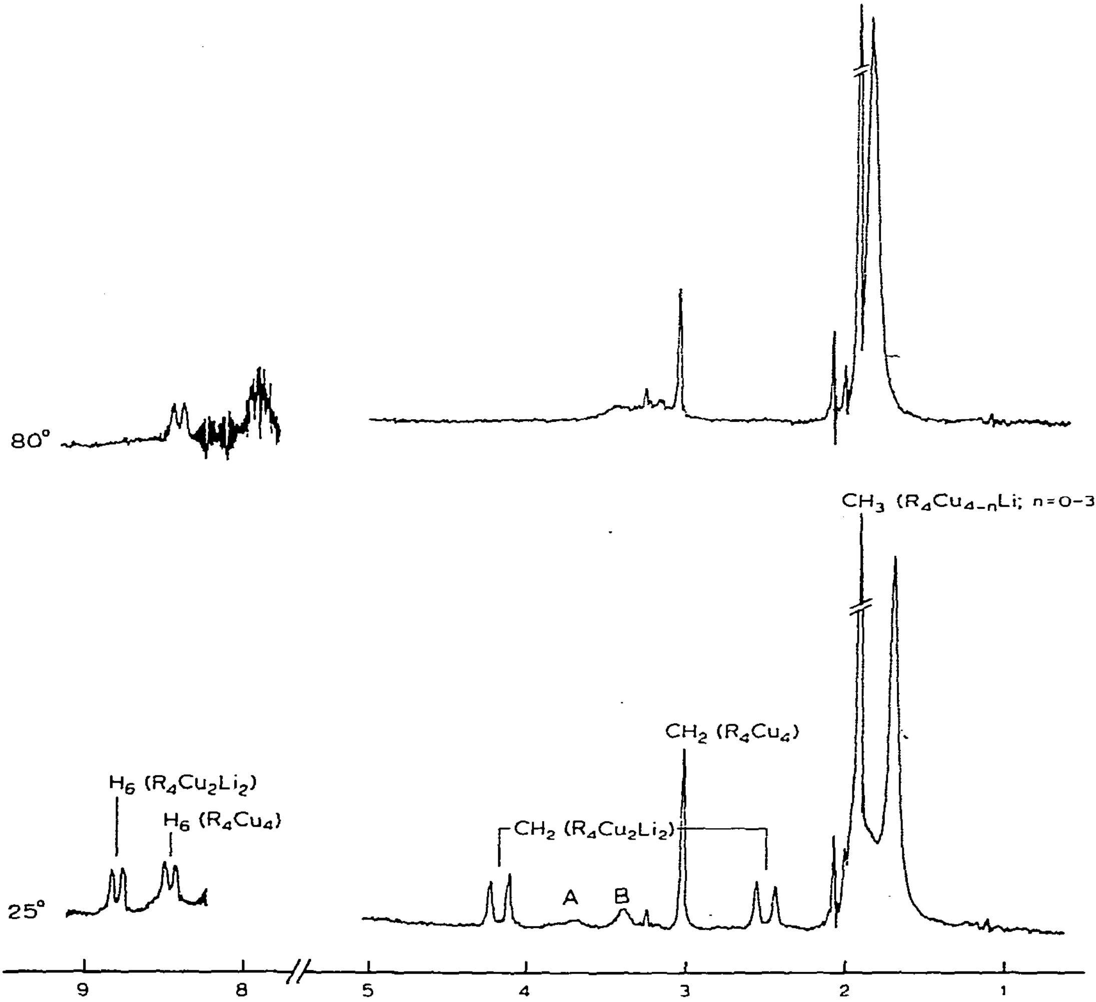

Fig. 3. ^1H NMR spectra (δ, ppm) of the 1/1 mixture of Ar_4Cu_4 (IX) and $Ar_4Cu_2Li_2$ (IV) in C_6H_6.

rings in the 3*c*—2*e* bond around C(1)—C(4) *. Therefore, the observed coalescence of the NCH_2 patterns in the present $Ar_4Cu_4/Ar_4Cu_2Li_2$ solution indicates that this must be due to rapid (on the NMR timescale) interaggregate exchange between $Ar_4Cu_2Li_2$ and the species A and B. When the heated solution was cooled to room temperature, the original spectrum was obtained. This indicates that at higher temperatures exchange between the respective aggregates is accelerated, and that the exchange process rapidly approaches equilibrium at each temperature.

The aggregation state of the species A and B, which are in equilibrium with $Ar_4Cu_2Li_2$ and Ar_4Cu_4, is not known. However, on the basis of the observation

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* Full details of these intramolecular dynamic processes taking place in $Ar_4M_2Li_2$ species are given in ref. 23. A preliminary account of this work which concerns the relation between these dynamic processes and the kinetic stability of the 3*c*—2*e* aryl—metal interaction has been given in ref. 36.

that the 2-[(dimethylamino)methyl]phenyl-metal-IB, -metal-IB-lithium and lithium compounds are tetranuclear species, one would intuitively assume that A and B are the tetranuclear mixed species Ar_4Cu_3Li and Ar_4CuLi_3.

Mechanistic aspects of the exchange reactions in the $Ar_4M_4/Ar_4M_2Li_2$ systems

Brown et al. [37] have elegantly shown that exchange reactions between polynuclear organolithium compounds involve associative or dissociative pathways of species $(alkyl)_nLi_n$ rather than exchange via alkyl anions by studying the exchange of mixtures of isotopically pure $t\text{-}Bu_4{}^6Li_4$ and $t\text{-}Bu_4{}^7Li_4$ in cyclopentane. The latter exchange reaction leads to the formation of all the possible mixed species $t\text{-}Bu_4{}^6Li_n{}^7Li_{4-n}$ ($n = 1, 2, 3$).

Exchange between the tetranuclear arylcopper Ar_4Cu_4 and arylcopperlithium species may likewise proceed via pathways involving dissociation or association, e.g.:

(i) Dissociation to a binuclear intermediate, e.g.:

$$\begin{array}{lll} Ar_4Cu_2Li_2 & \rightleftharpoons 2\,Ar_2CuLi & \\ & & Ar_2CuLi + Ar_2Cu_2 \rightleftharpoons Ar_4Cu_3Li \\ Ar_4Cu_4 & \rightleftharpoons 2\,Ar_2Cu_2 & \end{array}$$

(ii) Dissociation followed by association to a hexanuclear intermediate, e.g.:

$$Ar_4Cu_2Li_2 \rightleftharpoons 2\,Ar_2CuLi$$

$$Ar_4Cu_3Li + Ar_2CuLi \rightleftharpoons [Ar_6Cu_4Li_2] \rightleftharpoons \underset{\text{“}cis\text{” isomer}}{Ar_4Cu_2Li_2} + Ar_2Cu_2$$

$$\begin{array}{ccc} \underset{\text{“}cis\text{” isomer}}{Ar_4Cu_2Li_2} + Ar_2CuLi \rightleftharpoons & [Ar_6Cu_3Li_3] & \rightleftharpoons Ar_4CuLi_3 + Ar_2Cu \\ & \updownarrow & \\ & Ar_4Cu_3Li + Ar_2Li_2 & \end{array}$$

(iii) Association of two tetramers to an octanuclear intermediate, e.g.:

$$Ar_4Cu_4 + \underset{\text{“}trans\text{” isomer}}{Ar_4Cu_2Li_2} \rightleftharpoons [Ar_8Cu_6Li_2] \rightleftharpoons 2\,Ar_4Cu_3Li$$

$$\begin{array}{ccc} Ar_4Cu_3Li + Ar_4Cu_2Li_2 \rightleftharpoons & [Ar_8Cu_5Li_3] & \rightleftharpoons Ar_4CuLi_3 + Ar_4Cu_4 \\ & \updownarrow & \\ & \underset{\text{“}cis\text{” isomer}}{Ar_4Cu_2Li_2} + Ar_4Cu_3Li & \end{array}$$

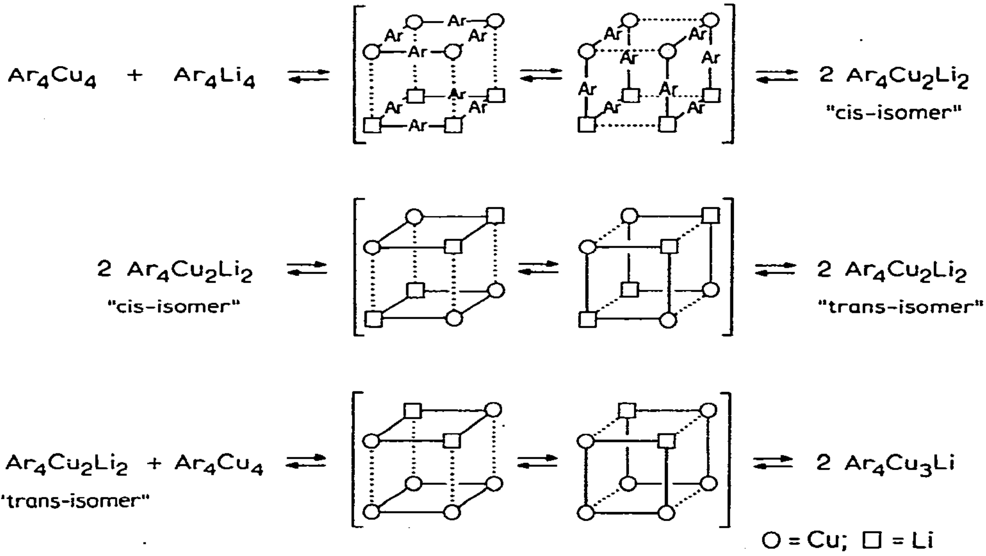
Further dissociation of the binuclear species into mononuclear species would not significantly change the discussion. However, formation of such species seems unlikely in view of the copper atom becoming highly coordinatively unsaturated when going from a binuclear to a mononuclear structure. In this respect, it is important to note that this discussion relates to exchange processes taking place in non-coordinating solvents such as benzene or toluene.

Dissociation of the polynuclear species taking place in both (i) and (ii) necessarily involves rupture of the rather stable aryl-bridge bond. Alternatively, pathway (iii), which involves the formation of an octanuclear intermediate $Ar_8Cu_{8-n}Li_n$ directly by association of two tetranuclear species, makes complete aryl—metal bond rupture unnecessary, and would therefore provide an attractive explanation for the interaggregate exchange reactions. Several observations in organocopper chemistry demonstrate this. For example, Cairncross and Sheppard isolated the stable octanuclear arylcopper compound $(m\text{-}F_3CC_6H_4\text{-}Cu)_8$ [38]. ^{19}F NMR spectroscopy revealed that the $m\text{-}F_3CC_6H_4$ groups are mobile in this octamer. Furthermore, tetranuclear arylcopper compounds undergo slow interaggregate exchange [cf. eqn. $Ar_4Cu_4/(4\text{-}MeAr)_4Cu_4$ and refs. 20, 35]. This is particularly interesting for $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ the tetranuclear structure of which does not break down in the presence of monodentate ligands [39].

In Scheme 2 some of the possible interaggregate exchange steps each involving octanuclear intermediates are shown. This scheme applies for both the simple arylcopperlithium species and the species containing built-in ligands. In the octanuclear intermediate the 3*c*—2*e* bonded aryl groups are mobile. The symmetry of the electron deficient bond allows the aryl group to change edges of the central $Cu_{8-n}Li_n$ cube without C—M bond rupture (see Fig. 4A).

Taking the hybridization at the M atoms into account, which is either digonal or trigonal, this process must be a concerted edge—corner—edge migration involving all eight aryl groups. The fact that all eight aryl groups are included in the process points to a considerable energy barrier to interaggregate exchange. This is in line with the observation that this exchange is in the slow-exchange limit on the NMR timescale. In this respect this process of intra-aggregate exchange of sites by the aryl groups is reminiscent of the processes via which CO groups are mobile in metal carbonyl clusters [40].

The migration of aryl groups involves a reversible change of the 3*c*—2*e* ArM_2 into a 2*c*—2*e* ArM bonding situation (note that Au(9) and Au(11) clusters have



SCHEME 2. Possible interaggregate exchange steps for tetranuclear arylmetal species Ar_4M_4 involving octanuclear intermediates Ar_8M_8.

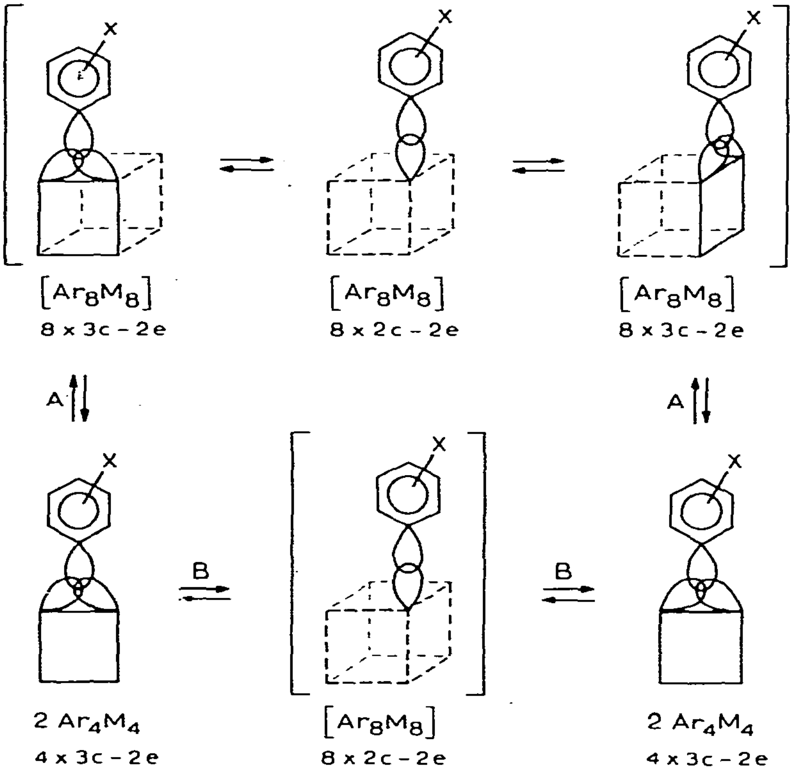


Fig. 4. Possible processes for the interaggregate exchange of aryl groups between tetranuclear arylmetal species Ar_4M_4.

a similar Au—Au—X arrangement [41]). Process B in Fig. 4 represents a second possibility. This differs from process A in the way in which the aryl groups change edges. Association of the two tetranuclear species having 3*c*—2*e* bonded aryl groups results in formation of an octanuclear intermediate with eight 2*c*—2*e* corner M—aryl interactions. Dissociation of the octanuclear intermediate into the two tetranuclear species reestablishes the 3*c*—2*e* M_2—aryl bonding situation.

The pathways shown in Scheme 2 and Fig. 4 may provide a low energy pathway for exchange leading to $Ar_4Cu_2Li_2$ as well as the mixed species Ar_4Cu_3Li and Ar_4CuLi_3. Finally, it must be emphasized that exchange between the various aggregates is strongly influenced by the presence of the built-in ligand. The tendency of the 2-Me_2NCH_2 (as well as the NMe_2) ligand to form coordination bonds with lithium rather than with copper strongly influences the product ratio in the equilibrium mixture at room temperature. ^{1}H NMR studies of the dynamics of the Ar group in $Ar_4M_2Li_2$ species have shown that at this temperature dissociation of the Li—N bond is slow on the NMR time-scale [23]. Thus the *trans*-$Ar_4M_2Li_2$ structure is more stable than all other possible tetranuclear species because of the Li—N interaction. However, at higher temperatures this coordinative interaction is less important, and also makes the mixed Cu_3Li and $CuLi_3$ species more probable.

Reactivity—structure relationships

The reactivity of organocuprates used in organic synthesis has usually been discussed in terms of the participation of anionic species R_2Cu^- in the reaction (cf. refs. 2). In view of the great difference in chemical reactivity between RCu and RLi—CuX or RCu—RLi reagents, e.g. in C—C coupling reactions with α,β-unsaturated carbonyl compounds, it is surprising that little attention has been given to the role of the lithium atom in bringing about the change in reactivity.

We have previously shown that in arylcopperlithium compounds the lithium atom is the coordinatively unsaturated site [3,4,15]. In our opinion this is not given full recognition in mechanistic discussions of reactions in which these species are involved. *p*-Tolylcopperlithium is insoluble in benzene [15]. Careful addition of ether gives the tetranuclear *p*-$Tol_4Cu_2Li_2 \cdot 2\ OEt_2$ compound in which the ether molecule becomes coordinated to the lithium atom. The metal-IB atom is two coordinate and does not react further with external ligands such as PPh_3, as shown by the isolation of *p*-$Tol_4Au_2Li_2 \cdot 2\ OEt_2$ from the reaction of $BrAuPPh_3$ with *p*-TolLi [15]. Furthermore, slow addition of THF to benzene solution of $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ reveals that the THF molecules compete with the built-in ligand for coordination sites at lithium. This was concluded from the dynamic NMR pattern of the 2-Me_2NCH_2 ligand. In agreement with the stabilization of the *trans*-isomer by the $CH_2(Me_2)N$—Li coordination (see Fig. 3), this competing process is accompanied by formation of the other possible tetranuclear aggregates $(2\text{-}Me_2NCH_2C_6H_4)_4M_{4-n}Li_n$, $n = 1$ or 3 (see Fig. 3). We suggest that anchoring of the substrate to organocuprate species takes place at lithium and not at the copper site (cf. refs. 3 and 42). Furthermore, the lack of coordination by phosphine ligands at the copper atoms of organocuprates accounts for the absence of asymmetric induction in reactions of cuprates which were carried out in the presence of chiral phosphines [39].

The course of the reactions of organocuprates with organic molecules is greatly influenced by the nature of the organic groups present. In reactions of mixed organocopperlithium reagents $(R_tRCuLi)_n$ in which R is C≡CR, CN, SR, etc. the group R_t (alkyl or aryl) is selectively transferred, whereas the ligands R do not participate in the reaction [2]. The ability of these reagents to transfer one ligand R_t selectively can be rationalized. If, on the basis of the structural features of the organocuprates discussed in this paper, it is accepted that the cuprate reagents are cluster compounds with bridging organo ligands, then it is to be expected that their reactivity in cross coupling and conjugate addition reactions will increase with decreasing binding ability of the organo ligand [3,4]. Thus, the tendency towards transfer will decrease in the sequence alkyl > aryl > C≡CR > C≡N. For example in reactions of $Me_4Cu_2Li_2$ compounds with aryl iodides metal—halogen exchange constitutes a serious problem [2]. This can be explained in terms of nucleophilic attack of the bridged Me group on the I atom of ArI, affording MeI and the more stable aryl-bridged CuLi cluster. Furthermore, in such reactions CuI or LiI is formed which enters into interaggregate exchange with the cuprate species present in the reaction mixture resulting in $(Me_{2-n}CuLiI_n)_m$ species. This implies that during the reaction the concentration of the active aggregate of the MeCu—MeLi or MeLi—CuX reagents decrease. This may provide an explanation for the large excess of reagent required in reactions of organocuprates. We have recently demonstrated the influence of side reactions (e.g. halogen—metal exchange, formation of CuI, etc.) leading to mixed clusters $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CR)_2$ and $(2\text{-}Me_2NC_6H_4)_4$-Cu_6I_2 in the cross-coupling reactions of $2\text{-}Me_2NC_6H_4Cu$ with $IC{\equiv}CR$ or of $2\text{-}Me_2NC_6H_4I$ with $CuC{\equiv}CR$ [43].

Experimental

General remarks

All reactions were carried out under dry oxygen-free nitrogen.

The NMR spectra were recorded on Varian Associates T-60 (^{1}H), HA-100 (^{1}H) and XL-100/15 FT (^{13}C) NMR spectrometers.

Elemental analyses were carried out in the Analytical Department of the Institute for Organic Chemistry TNO.

The starting aryllithium and metal-IB compounds were prepared by published methods: $2\text{-}Me_2NCH_2C_6H_4Li$ [44], —Cu [19,44], —Ag [45]; $2\text{-}Me_2NCH(Me)$-C_6H_4Li [18], —Cu [18,23], —Au [18,23]; $2\text{-}Me_2NC_6H_4Li$ [27], —Cu [44], —Au [22]; $(2\text{-}Me_2NCH_2C_6H_4)_4Ag_2Li_2$ [5].

Synthesis of bis{2-[(dimethylamino)methyl]phenyl}copperlithium (IV) (via ArLi/CuBr 2/1)

Solid cuprous bromide (29.6 mmol) was added during $1\frac{3}{4}$ h to a well stirred suspension (kept at —20°C) of 59.2 mmol of 2-[(dimethylamino)methyl]-phenyllithium (I) in ether (120 ml). The mixture was stirred at —20°C for an additional 1 h, allowed to warm to room temperature (1 h), and then stirred for another 2 h. The resulting mixture (white and black precipitates and a light-brown solution) was cooled to —78°C then quickly filtered. The precipitate was washed with ether (3 × 20 ml) and dried in vacuo affording a grey residue (A). Concentration of the filtrate by low temperature distillation at low pressure yielded a light-brown residue (B). A and B were worked-up separately.

Work-up of A. Residue A was transferred to a centrifuge tube, benzene (60 ml) was added, and the suspension was stirred for 1/2 h. Centrifugation (2500 rpm; 10 min) of the suspension afforded a black precipitate and a light-brown solution. The solution was decanted. The solvent was distilled back into the centrifuge tube leaving a light-brown solid (4.25 g). This was recrystallized from benzene as follows: benzene (6 ml) was added and the suspension was stirred at 40°C for 1/2 h, the solution was then decanted into a second flask. The benzene was distilled back leaving an almost white residue (C). This procedure (stirring at 40°C, decantation, back-distillation) was repeated 3 times. The white solid (C) was dissolved at 40°C in benzene (about 14 ml) and pentane (about 20 ml) was added until cloudiness appeared. The resulting solution was slowly cooled to 4°C, affording white crystals of IV. The solution was decanted and the crystals washed with pentane affording white crystalline IV in 11% yield. (Found: Cu, 18.9. $C_{18}H_{24}N_2CuLi$ calcd.: Cu, 18.75%).

From the benzene/pentane solution another portion of almost pure IV (22% yield) was isolated.

Work-up of B. Residue B was extracted with benzene (by the centrifugation procedure described above) affording a white, benzene-insoluble residue (quantitative amount of LiBr). The benzene extract was concentrated to give a white sticky residue. Extraction of the residue with pentane yielded almost pure IV. Recrystallization afforded white crystalline IV in 18% yield. (Found: Cu, 18.8. $C_{18}H_{24}N_2CuLi$ calcd.: Cu, 18.75%.)

Synthesis of bis{5-methyl-2-[(dimethylamino)methyl]phenyl}copperlithium (V) (via ArLi/ArCu 1/1)

5-Methyl-2-[(dimethylamino)methyl]phenyllithium (II) (7.33 mmol) was dissolved in benzene (15 ml), and a suspension of the organocopper (X) (7.33 mmol) in benzene (15 ml) was added. The heterogeneous mixture was stirred for 24 h, yielding a yellow-brown solution with a white precipitate. The solution was decanted into a second flask. The benzene was distilled back onto the white precipitate. This extraction was repeated three times. To the benzene extract (15 ml), which already contained a white crystalline precipitate, pentane (15 ml) was added. The pentane/benzene solution was decanted, and the solid was washed with pentane. The pentane was decanted and the white solid (V) was dried in vacuo. Yield 50%. (Found: Cu, 18.4. $C_{20}H_{28}N_2CuLi$ calcd.: Cu, 17.32%.)

Synthesis of 2-[(dimethylamino)methyl]phenyllithium (I)

N,N-Dimethylbenzylamine (20 mmol) was added to a solution of butyllithium (20 mmol) in ether/hexane (65/10 v/v) and the resulting yellow solution was stirred for 3 days, during which a white solid (I) crystallized. This was isolated in the following way: the ether solution was decanted into a second flask and the ether condensed back onto the white crystals. The crystals were thoroughly washed and the ether again decanted. This procedure was repeated three times, and the solid was then dried in vacuo. Yield 78%. (I) starts to decompose at about 129°C. Its IR spectrum was identical to that reported in ref. 34.

Synthesis of {5-methyl-2-[(dimethylamino)methyl]phenyl}lithium (II)

A 1/1 mixture of *N,N*-dimethyl(4-methylbenzyl)amine and butyllithium (60 mmol) in ether/hexane (125/32 v/v) was stirred for 3 days. The resulting yellow solution was concentrated to about 30 ml and then set aside at —20°C for 24 h. Very finely devided crystalline II separated. The solution was decanted The white solid was washed with pentane (3 X 20 ml, see above) giving white II in 80% yield. Decomposition at 170—175°C. NMR (C_6D_6, TMS internal, δ ppm); 1.31 and 1.86 (2 s, NCH_3, 6 H), 2.31 (s, 5-CH_3, 3 H), 2.93 and 4.49 ($2 \times$ d, $J_{gem} \simeq 13$ Hz, NCH_2, 2 H), 7.01 (2 d, $J_{3,4} \simeq 7$ Hz, $J_{4,6} \simeq 2$ Hz, 1 H), 7.05 (d, H_3, 1 H) and 8.17 (d, 1 H) (see Fig. 1 in ref. 23).

Synthesis of bis{2-[(dimethylamino)methyl]phenyl}goldlithium (VII)

To a suspension of I (40 mmol) in ether (150 ml), solid $BrAuPPh_3$ (20 mmol) was slowly added. The resulting light purple coloured suspension was stirred at room temperature for 8 h. The precipitate was separated by centrigugation, washed with ether (3 X 40 ml) and dried in vacuum. The resulting solid was dissolved in benzene (80 ml) and the solution filtered through a small layer of alumina. The filtrate was concentrated to a small volume (±10 ml).

VII precipitated upon addition of pentane (100 ml). White VII was filtered off, washed with pentane and dried. Yield 52%. Mol. wt., see Table 2. Anal.: Found: C, 45.0; H, 5.3; Au, 41.5; N, 5.9. $C_{18}H_{24}AuLiN_2$ calcd.: C, 45.78; H, 5.12; Au, 41.70; N, 5.93%. ^{1}H NMR data, see Table 4; PPh_3 absent.

For the synthesis of bis{[1-(*S*)-(dimethylamino)ethyl]phenyl}goldlithium [(*S*)-VIII], which was carried out along the lines described for VII, see ref. 18.

Synthesis of bis{2-[(dimethylamino)phenyl]}goldlithium (XV)

A solution of 2-(dimethylamino)phenyllithium (52 mmol) in ether (150 ml) was added during 1/2 h to a suspension of $BrAuPPh_3$ (25 mmol) in ether (50 ml), and the resulting white suspension was stirred for 1 h. The precipitate was filtered off, washed with ether (removal of LiBr) then pentane, and dried. Yield 35%. Anal.: Found: C, 42.5; H, 4.6; Au, 43.7; N, 6.1. $C_{16}H_{20}AuLiN_2$ calcd.: C, 43.26; H, 4.54; Au, 44.34; N, 6.30%. Mol. wt., see Table 2. ^{1}H NMR in toluene-d_8: PPh_3 absent.

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