(3) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.
(4) Hertzer, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383.
(5) Novotny, M.; Lippard, S. J. *Chem. Commun.* **1973**, 202. See Lain, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127, for a more detailed report.
(6) Lewis, D. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1975**, *97*, 2697.
(7) Casanova, J., Jr.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.
(8) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351.
(9) Stephenson, T. A.; Bannister, E.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2538.
(10) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.
(11) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.
(12) This modification, which allows prescanning to omit weak reflections from the collection procedure, was devised by Dr. Phillip Fanwick.
(13) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.
(14) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed.; Wiley: New York, 1978; pp 136 and 154.
(15) Walton, R. A. "Proceedings of the Second International Conference on the Chemistry and Uses of Molybdenum"; Mitchell, P. C. H., Ed., Climax Molybdenum Co. Ltd.: London, 1976; p 34.
(16) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.
(17) Nimry, T.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 510.
(18) Brisdon, B. J.; Mialki, W. S.; Walton, R. A. Unpublished work.
(19) Nimry, T.; Urbancic, M. A.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 691.
(20) We plan to check this point in the near future, by carrying out the reactions between $Mo_2Cl_4(PR_3)_4$ and CO under high pressure conditions.
(21) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.
(22) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553.
(23) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

Stereochemistry of Arylmetal-1B, Aryllithium, and Arylmetal-1B-Lithium Clusters $Ar_4M_2Li_2$ (M = Cu, Ag, or Au). Detection of Rotation of Three-Center Two-Electron Bonded Aryl Groups around the C(1)–C(4) Axis[1a]

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Abstract: Arylmetal-1B, aryllithium, and arylmetal-1B-lithium compounds have polynuclear structures consisting of a metal core to which each of the aryl groups is bound via C(1) to two metals by a three-center two-electron (3c-2e) bond. When the metals are unlike and aryl is dissymmetrically substituted C(1) is a center of chirality. Rotation of the aryl group around the C(1)···C(4) axis causes a continuous inversion of configuration at C(1). Dynamic ^1H and ^{13}C NMR studies revealed that the prochiral methylene group in 2-$(Me_2NCH_2)C_6H_4$-metal compounds $Ar_4M_2Li_2$ (M = Cu, Ag, or Au) is an excellent probe for the monitoring of the configuration at C(1) in each of the 2-$(Me_2NCH_2)C_6H_4MLi$ units. In this way the rotation of 3c-2e bonded aryl groups around the C(1)···C(4) axis has been established for the first time. Introduction of a second center of chirality of which the configuration cannot invert allows the detection of the stereochemistry of the $Ar_4M_2Li_2$ aggregates. The use of the chiral 2-$Me_2NCH(Me)$ rather than the prochiral 2-Me_2NCH_2 group as a built-in ligand provided unambiguous proof for the occurrence of Cu–N coordination in the Ar_4Cu_4 compounds at low temperature. Formation of Cu–N coordination bonds in the Ar_4Cu_4 cluster having C_2 symmetry constitutes a second element of chirality which in combination with the chirality at the benzylic C atoms gives rise to two distinguishable stereoisomers of Ar_4Cu_4. Li–N coordination in $[5\text{-Me-2-}(Me_2NCH_2)C_6H_4]_4Li_4$, which likewise constitutes an element of chirality, could be detected by ^1H and ^{13}C NMR. The novel results concerning the dynamics of 3c-2e bonded aryl groups at the same time provide a rationale for the kinetic stability order of the ortho-substituted arylmetal-1B clusters: 2-$Me_2NC(Z)HC_6H_4$ (Z = H or Me) $\approx$ 2-$Me_2CHCH_2C_6H_4$ $\approx$ 2-$Me_2NC_6H_4$ $\approx$ 2,6-$(MeO)_2C_6H_3$ $\approx$ 2,6-$Me_2C_6H_3$ > 2-MeC_6H_4 > 4-MeC_6H_4 $\approx$ unsubstituted phenyl-M cluster.

Introduction

Considerable information concerning the structure of homo- and heteronuclear arylcopper, -silver, and -gold compounds has recently become available (see ref 6-9). The presence of a central metal core to which aryl groups are bonded via 3c-2e bonds appears to be a persistent structural feature for these compounds. In the simple arylcopper tetramers, e.g., 4-$tolyl_4Cu_4$,[7] the aryl groups bridge the Cu_2 edges of an arrangement of four Cu atoms, which, as a result of linear hybridization at Cu (cf. the structure of $(Me_3SiCH_2)_4Cu_4)$,[10] has a planar configuration. In the presence of built-in ligands (cf. the structure of $(5\text{-Me-}Me_2NCH_2C_6H_3)_4Cu_4)$, the Cu_4 core has a butterfly-type configuration which is a consequence of the almost planar trigonal coordination geometry of the Cu atoms[11,12] The X-ray analysis further revealed a dihedral angle of about 80° between the aryl nucleus and the plane through the bridged metals and the bridging atom.

In this paper we present a qualitative study of the dynamic behavior in solution of 3c-2e bonded aryl groups present in polynuclear aryllithium, arylmetal-1B, and arylmetal-1B-lithium compounds. This study is related to the problem of stabilization of the configuration of chiral centers by intramolecular coordination. Recently, we have studied the latter problem using $(2\text{-}Me_2NCH(Z)C_6H_4)PhMeSnBr$ (Z = H or (*S*)-Me) as model compounds.[13]

Outline of the Dynamic Process

Bonding of Ar in Ar_4M_4 and $Ar_4M_2Li_2$. The proposed bonding in arylmetal-1B clusters[9,12] is schematically shown in Figure 1. The molecular orbital, which is lowest in energy, results from overlap of hybrids of s and p orbitals on copper (depending on the coordination symmetry, sp or sp^2) and a carbon sp^2 orbital. The second molecular orbital involves overlap of a carbon p_z orbital with an antisymmetric combination of Cu orbitals.

In the solid the aryl nucleus occupies a position almost perpendicular to the Cu–Cu vector.[9,12] Taking into account the bonding scheme in Figure 1, rotation of the aryl nucleus

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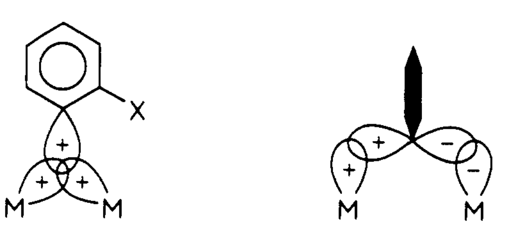

Figure 1. Molecular orbitals involved in the 3c-2e ArM_2 bonding.

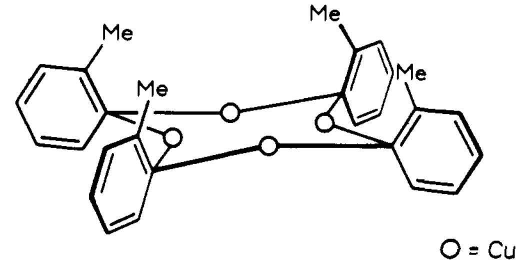

Figure 2. One of the stereoisomers of $(2\text{-tolyl})_4Cu_4$.

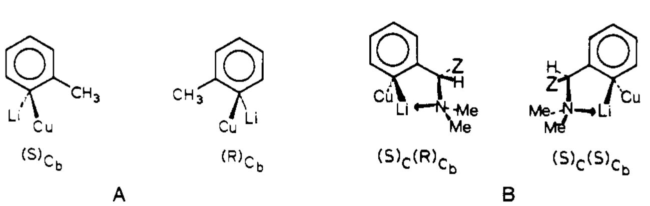

Figure 3. Pairs of one rotamer configuration for a dissymmetrically substituted 3c-2e bonded aryl group: (A) in $2\text{-Tol}_4Cu_2Li_2$; (B) in $(2\text{-}Me_2NCHZC_6H_4)_4Cu_2Li_2$.

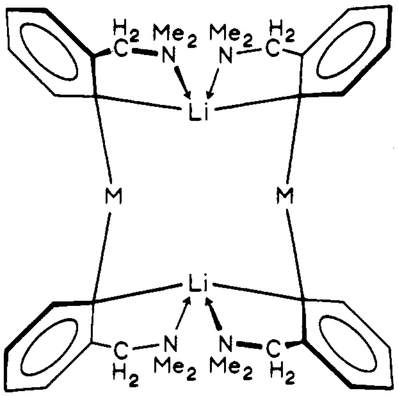

Figure 4. Schematic structure of the $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ (M = Cu, Ag, or Au) compounds.

around the C_b-C(4) axis must be expected to occur in solution. In each of the possible rotamers overlap in the first MO will be equal. In case bulky substituents are present in the position ortho to C_{bridge}, rotamers having the plane of the aryl ring about perpendicular to the Cu-Cu axis will become more stable. Moreover, in the latter rotamers overlap of the antisymmetric metal orbital combination with the carbon p_z orbital will be maximal, which further lowers the energy of these rotamers. Recent calculations by Clark and Schleyer indicated a preferential stabilization of the transition state for inversion of alkyl groups in alkyllithium aggregates $(RCH_2Li)_2$.[14] In the transition state a carbon orbital of a planar methyl group interacts with an antisymmetric combination of lithium s orbitals.

Stereoisomerism in Ar_4M_4 and $Ar_4M_2Li_2$. In principle, Ar_4M_4 and $Ar_4M_2Li_2$ compounds containing dissymmetrically substituted aryl groups can exist as four unique stereoisomers (see Figure 2). These stereoisomers are detectable by NMR spectroscopy because they will have different chemical shifts. Indeed, for 2-tolylcopper tetramer multiplet resonance patterns have been detected at low temperature[15] which were ascribed to the presence of such isomers.[16] The observation that these multiplets coalesce at higher temperatures was presented as evidence for the occurrence of rotation of the 3c-2e bonded 2-tolyl groups[16] (cf. ref 17). This interpretation is correct only in the case that inter- and intraaggregate exchange processes are slow on the NMR time scale. However, the presented NMR data[16] do allow the conclusion that the 2-tolylcopper tetramers can be frozen out in various stereoisomers.

Local Environment Concept in $Ar_4M_2M'_2$ Clusters. C_{bridge} of a dissymmetrically substituted 3c-2e bonded aryl group, which bridges two unlike metal centers, represents a chiral center.[18] Two cases may be distinguished: (1) the two metal atoms are different as in our $2\text{-}Me_2N$- and $2\text{-}Me_2NCH_2$-substituted arylmetal-1B-lithium compounds[8,21-23] as well as in hexanuclear $(2\text{-}Me_2NC_6H_4)_4M'_2M_4X_2$ ($M' \neq M$ = Cu, Ag, or Au)[8] and (2) the metal atoms are similar but differ with respect to their coordination geometry (e.g., the apical and equatorial metal atoms in $(2\text{-}Me_2NC_6H_4)_4M_6X_2$, M = Cu[24] or Ag[25]). *Rotation of the 3c-2e bonded aryl group around the C_b-C(4) axis will cause a continuous inversion of configuration at C_{bridge}.* For this process at C_{bridge} which does not involve rearrangement of bonds by stereoisomerization or bond dissociation-association (e.g., S_N2 or S_N1) processes we propose the term fluxional chirality. Figure 3A shows the enantiomeric pair $(S)_{C_b}$ and $(R)_{C_b}$[26] for one rotamer conformation in the limiting situation in 2-tolylcopperlithium $(2\text{-Tol}_4Cu_2Li_2)$. When considering the "local environment" of one ArMLi unit instead of the total geometry of the $Ar_4M_2Li_2$ cluster, inversion of configuration at C_{bridge} becomes detectable by NMR spectroscopy when the substituent present in Ar is prochiral.

The CH_2 group in $2\text{-}Me_2NCH_2C_6H_4$ represents such a prochiral center (see Figure 3B; Z = H). In the limiting situation the CH_2 protons are diastereotopic and are expected to appear in the ^1H NMR spectrum as an AB pattern which will coalesce to a singlet if inversion at C_{bridge} [i.e., rotation around C_b-C(4)] is rapid on the NMR time scale. Replacement of the methyl group in 2-TolCuLi by the sterically more demanding $2\text{-}Me_2NCH_2$ group will result in an increased barrier to rotation of the aryl ring. Furthermore, coordination of the Me_2N group with one of the bridged metal atoms fixes the phenyl ring in an almost perpendicular position. This metal-nitrogen coordination renders the N atom a stable prochiral center which offers a second probe reflecting the dissymmetry at C_{bridge}. Therefore, NMR spectroscopy in principle allows the separate detection of M-N coordination and rotation of the aryl groups in these compounds.[27] It is important to note that in the $(2\text{-}Me_2NCH_2C_6H_4)MLi$ units shown in Figure 3B rotation of the aryl nucleus is only possible if the metal-N bond is dissociated, i.e., inversion of configuration at C_{bridge} can only take place in the noncoordinated situation.

Dynamic Behavior of the Aryl Groups in $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ Clusters (M = Cu, Ag, or Au)

The ArMLi Unit. In the $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ (M = Cu, Ag, or Au) clusters *each of the four aryl groups bridges one metal-1B and one lithium atom* (Figure 4; for a discussion see ref 21 and 28). Thus four ArMLi units are present.

In contrast with the existing uncertainty concerning the role of inter- or intraaggregate exchange processes in the dynamics of the 2-Tol_4Cu_4 compounds (see above) ^{13}C NMR data exclude such processes for compounds $Ar_4M_2Li_2$ (I-III). In $Ar_4Ag_2Li_2$ (II) the $J(^{107,109}Ag\text{-}^{13}C_b)$ and $J(^7Li\text{-}^{13}C_b)$ remain unaltered over the temperature range studied.[22] This points out that the 3c-2e ArAgLi bond remains intact on the NMR

Table I. ^{1}H NMR Spectra of $Ar_4M_2Li_2$ Compounds I-III and (*S*)-$Ar_4Au_2Li_2$

compd	δ, ppm^a			temp, °C (solvent)
	NCH_3 (T_{coal})	NCH_2 (T_{coal})	H_6	
$(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$	1.74 (s) (±5 °C)	4.12 (d), 2.48 (d) J_{gem} = 12 Hz (±90 °C)	8.74 (m, J_o = 7, J_m = 1.5 Hz)	25 (toluene-d_8)
	1.80 (s)	3.35 br	8.62 (m)	100
	1.26 (s), 1.89 (s)	4.12 (d), 2.35 (d)	8.85 (m)	−60
$(2\text{-}Me_2NCH_2C_6H_4)_4Ag_2Li_2$	1.74 (s) (±10 °C)^b	3.96 (d), 2.52 (d) (±90 °C)^c	8.66 (m)^d	25 (benzene-d_6)
$(2\text{-}Me_2NCH_2C_6H_4)_4Au_2Li_2$	1.79 (s) (±10 °C)	4.30 (d), 2.41 (d) J_{gem} = 12 Hz (±80 °C)	8.52 (m, J_o = 7, J_m = 1.5 Hz)	25 (benzene-d_6)
	1.82 (s)	3.58 (s)	8.42 (m)	80
((*S*)-$2\text{-}Me_2NCHMeC_6H_4)_4Au_2Li_2$	1.75 (s)(−10 °C)	0.88 (d),^{e} 4.84 (q)^f	8.62 (d of d, J_o = 7 Hz)^g	25 (benzene-d_6)
	1.27 (s, br), 2.10 (s, br)	0.82 (br),^{e} 4.76 (q, br)^f	8.60 (d, br)	−30 (toluene-d_8)

^{a} Me_4Si internal: s, singlet; d, doublet; m, multiplet. ^{b} Decoalesces into two singlets at 1.33 and 2.03 ppm. ^{c} Coalesces into singlet at 3.30 ppm. ^{d} Full assignment of the spectrum is discussed in ref 22. ^{e} α-CH, J = 7 Hz. ^{f} α-CH_3. ^{g} H_5 7.42 (t).

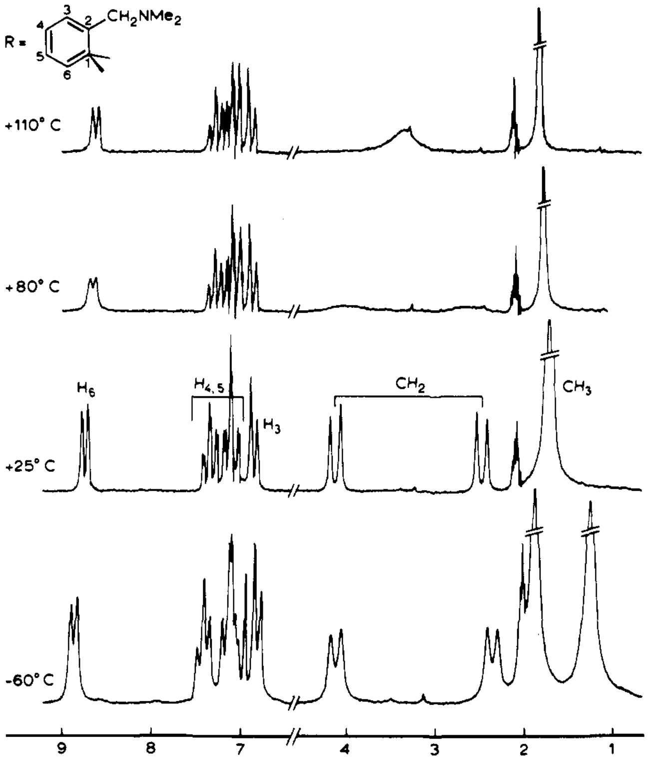

Figure 5. ^{1}H NMR spectra (δ ppm) of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ in toluene-d_8 at different temperatures.

time scale and that the observed dynamic processes must be related to rotation of the 3c-2e bonded aryl group around C_b-C(4). This observation clearly excludes processes involving interaggregate exchange via dissociation-association pathways as well as intraaggregate exchange processes by edge (3c-2e)-corner (2c-2e)-edge (3c-2e) migration[28,29] of the aryl groups. These conclusions can be extended to the copperlithium and goldlithium compounds because also for these compounds one $J(^{13}C_b\text{-}^7Li)$ of about 7 Hz is observed.[30]

The ^{1}H and ^{13}C resonance patterns for the benzylic and methylamino protons and C atoms for I-III are temperature dependent (see Figure 5 for the ^{1}H NMR spectra of I, Table I and tables in ref 2). The chemical shift differences between the three compounds are small. Characteristic features are the observation at low temperature of an AB pattern for the benzylic protons and two singlets for the methylamino protons. In the ^{13}C NMR spectrum two singlets are observed for the diastereotopic H_3CN carbon atoms below −20 °C. At room temperature these two singlets coalesce to one singlet. The coalescence temperatures for the benzylic and *N*-methyl ^{1}H resonance patterns in the ^{1}H NMR spectra in combination with the chemical shift differences (100-MHz spectra of I-III (CH_2), $T_c \approx 90$ °C, Δδ 1.6-1.9; (CH_3) T_c ±5 °C, Δδ 0.7 ppm) point out that two different processes, i.e., (1) Li-N dissociation and (2) rotation of the Ar group around C_b-C(4), are responsible for the dynamic behavior of the CH_2NMe_2 protons and carbon atoms (Figure 6).

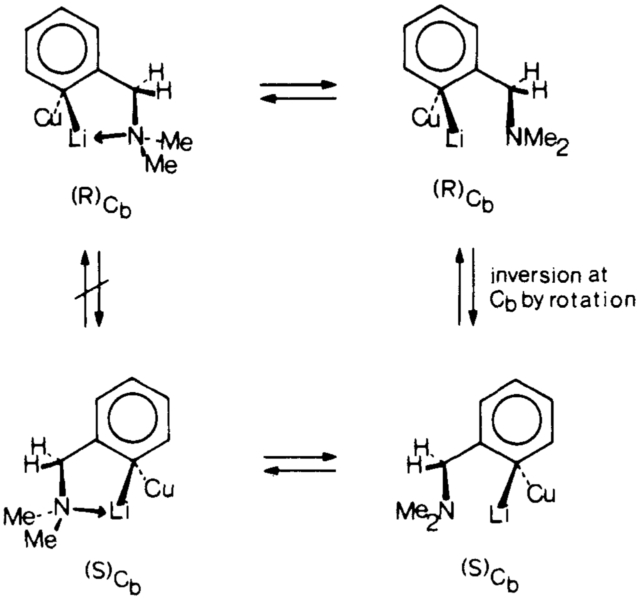

Figure 6. Scheme showing the Li-N dissociation-aryl rotation processes accounting for the spectra in Figure 5.

Going from −60 °C to higher temperatures the first process involves rate-determining N-Li bond dissociation, inversion at N, and concomitant C-N bond rotation followed by coordination. Pyramidal inversion at N as well as C-N bond rotation are low-energy processes with barriers amounting to 6 kcal/mol.[31] Consequently, the coupled inversion and C-N bond rotation processes are fast over the whole temperature range studied. The observation that the coalesced signal shifts downfield (0.14 ppm at 25 °C) with respect to the averaged position of the two NMe singlets at −60 °C and in the direction of the free amine confirms that the equilibrium $N_{coord} \rightleftarrows N_{free}$ shifts to the right (see Figure 5).

The AB pattern for the diastereotopic NCH_2 protons is still present up to 90 °C: see Figure 5. This indicates that inversion of configuration at C_{bridge} does not occur on the NMR time

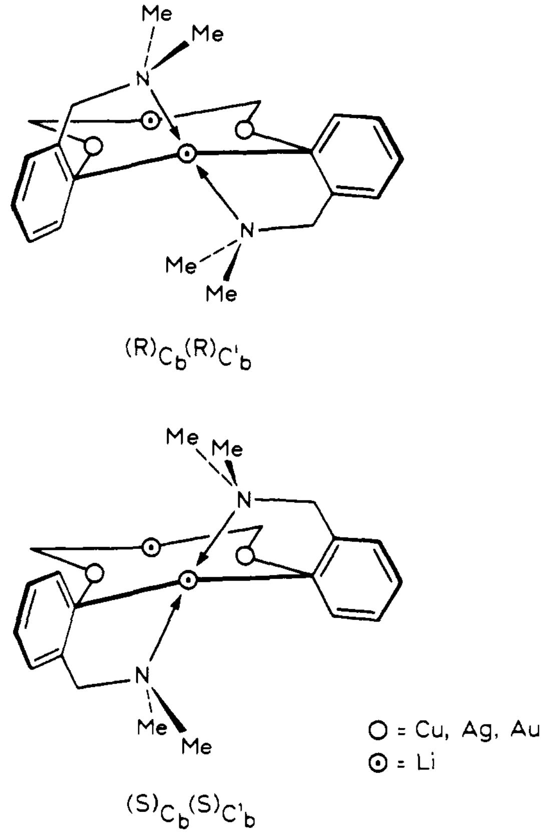

Figure 7. The configuration at C_{bridge} of two aryl groups bonded to the same Li atom in $(2\text{-}Me_2NCH_2C_6H_4)Cu_2Li_2$.

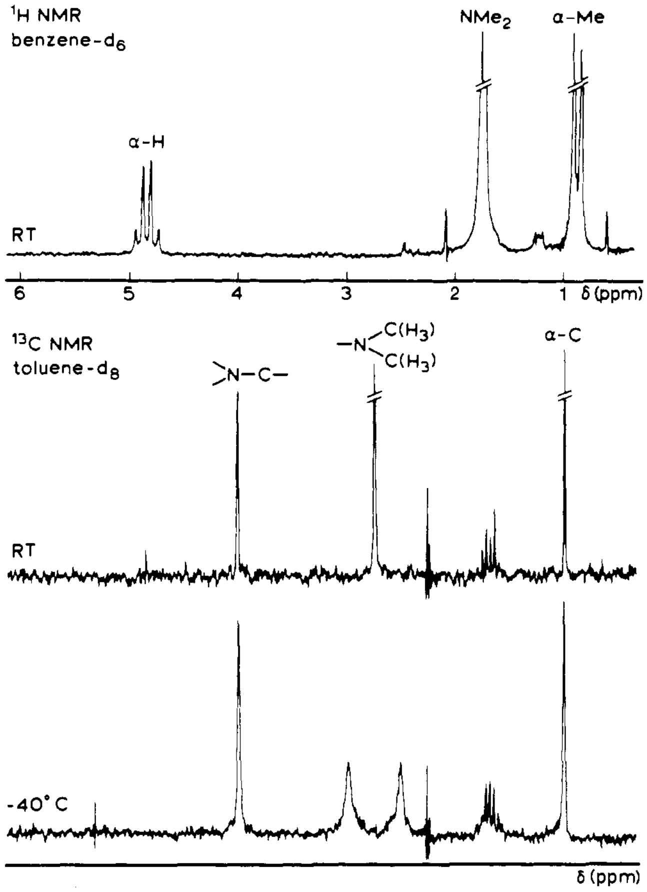

Figure 8. ¹H and ¹³C NMR spectra of $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Au_2Li_2$.

scale, which shows that rotation of the aryl group has become the rate-determining step. At 95 °C the CH_2 protons have become isochronous as a result of rapid rotation of the aryl group around the C_b-C(4) axis.

The $Ar_4M_2Li_2$ Cluster. So far we have considered the chiroptical properties of the ArMLi unit only. Combining the four units into an $Ar_4M_2Li_2$ aggregate in principle will result in a number of unique stereoisomers having different spectra. However, only one resonance pattern is observed at low temperature (cf. Figure 5), i.e., at the situation of inert Li-N coordination. This can be rationalized as follows.

The trans-metal arrangement as well as the preferential N-Li coordination restricts the number of possible stereoisomers. The configuration at the C_{bridge} centers of two aryl groups bonded to the same Li atom is either *S* or *R* as is shown in Figure 7.

Looking to the four metal atoms in $Ar_4M_2Li_2$ the possible combinations reduce to two enantiomeric pairs: *RR,SS/SS,RR* and *SS,SS/RR,RR*. Inspection of a model shows that the *SS,RR/RR,SS* enantiomeric pair can exist only if the four metal atoms are in one plane together with the bridging C atoms. This configuration has been observed in $Cu_4(CH_2SiMe_3)_4$ containing exclusively two-coordinate Cu atoms.[10] However, a planar configuration for $Ar_4M_2Li_2$ seems unlikely because of the presence of sp^3-hybridized lithium atoms in the M_2Li_2 core. In that case the bridging aryl groups will point alternately below and above the M-Li edges of the M_2Li_2 core. This would seem to eliminate the *SS,RR/RR,SS* enantiomeric pair and to leave the *SS,SS/RR,RR* pair as the only possibility. In order to study this problem of the configurations at the four C_{bridge} centers in the tetranuclear cluster in greater detail we have introduced a second chiral center in the substituent present in the aromatic ring. To this purpose examples of (*S*)-$Ar_4M_2Li_2$ and (*S*)-Ar_4M_4 in which (*S*)-Ar is (*S*)-2-$Me_2NCHMeC_6H_4$ were synthesized.

Dynamic Behavior of the Aryl Groups in $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Au_2Li_2$

$[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Au_2Li_2$ (V) has in solution the same structural features as the corresponding $Ar_4M_2Li_2$ compounds discussed above, i.e., a tetranuclear trans-metal core with the (*S*)-Ar groups each bridging one Li and one Au atom.[13,28]

The ¹H NMR spectra of V are temperature dependent. The NMe protons are diastereotopic below −22 °C[32] as are the C atoms of the NMe_2 group at −40 °C. The explanation for the observed dynamic behavior is the same as that given for the Me_2NCH_2 substituted derivatives, i.e., a coupled Li-N dissociation, (*S*)-Ar rotation around the C_b-C(4) axis. However, in this case more detailed information can be obtained about the configuration at C_{bridge} in the (*S*)-ArAuLi units. Introduction of a second center of chirality ($CHMeNMe_2$) of which the configuration cannot invert results in two diastereomeric forms, $S_{C_b}S_C$ and $R_{C_b}S_C$, of the (*S*)-ArAuLi units in V (see Figure 3B, Z = Me). This allows the detection of the stereochemistry at each of the C_{bridge} centers in the (*S*)-$Ar_4Au_2Li_2$ aggregates because the $S_{C_b}S_C$ and $R_{C_b}S_C$ units will have different resonance patterns.

The existence of a chiral C_{bridge} center (either *R* or *S*) in the ArMLi units of the $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ compounds was inferred from the observation of diastereotopic CH_2 protons which became enantiotopic by rapid rotation of the aryl group. It is therefore interesting that in '$[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Au_2Li_2$ only one configuration at C_{bridge} has been found; see Figure 8. This is clearly shown by the aliphatic part of the ¹³C NMR spectrum of V at −40 °C, which showed only one pattern.[33] At this temperature aryl rotation is blocked because of inert Li-N coordination [cf. two singlets for the (Me-N)C atoms]. Also in the ¹H NMR spectrum only one

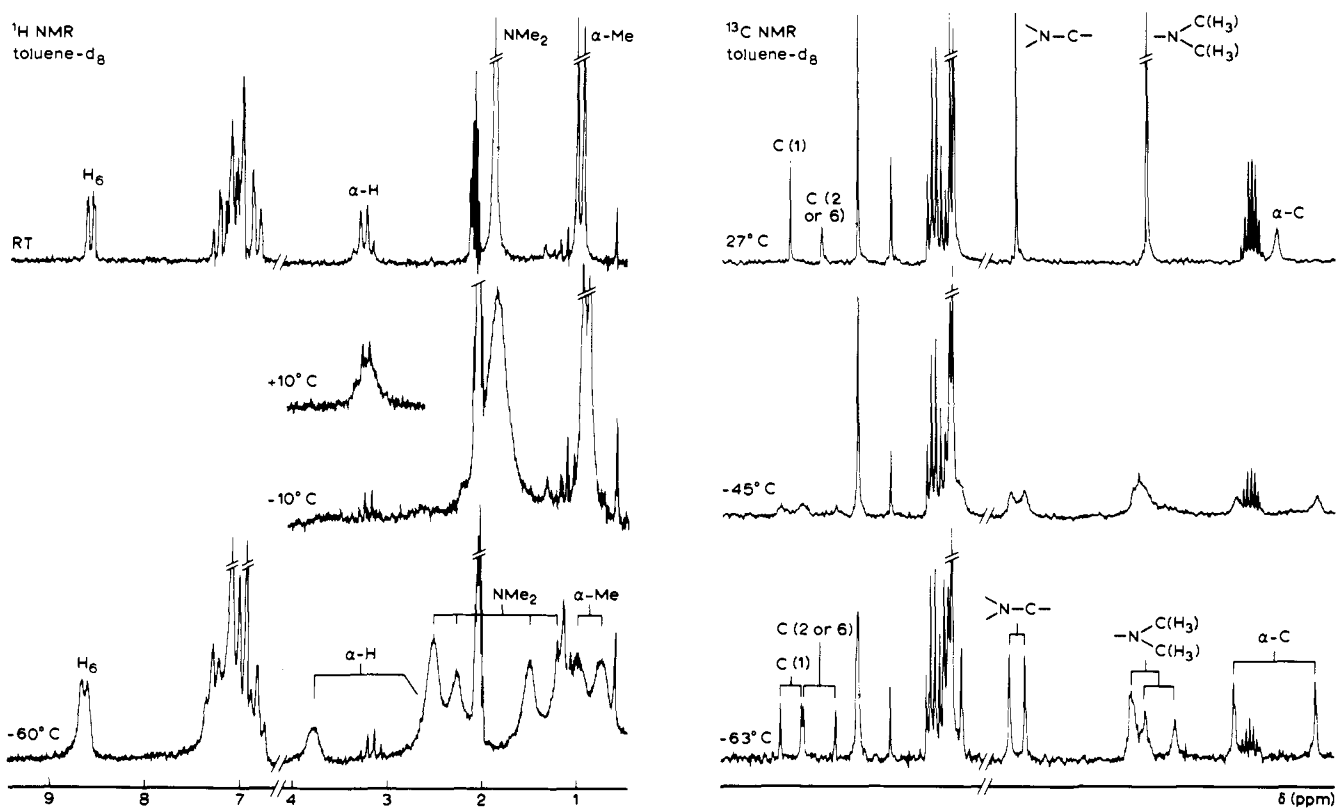

Figure 9. ^{1}H and ^{13}C NMR spectra of $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$.

Table II. ^{13}C NMR Data[a] of $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$ and $(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Li_4$

compd	δ, ppm NMe	NCH	5-Me	α-Me	$C_{(2)}$–$C_{(6)}$	$C_{(1)}$
$[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$[b]						
RT[c]	43.9	71.4		16.5	123.1. 123.2 123.9, 136.2 150.6	157.1
−63 °C	35.1, 41.4, 43.9 br	66.8, 70.1		22.6, 5.3	121.2, 123.1 123.6, 123.9 124.0, 124.8 147.5, 154.1	154.5, 158.9
$(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Li_4$[d]						
RT	42.9, 45.6	69.2	18.5		132.8 br, 139.9, 149.1	163.9 v br

[a] With ^{1}H decoupling, shifts relative to Me_4Si. [b] 0.7 g/4 mL of toluene-d_8. [c] For spectra at lower temperatures, see also Figure 9.

pattern is observed at 27 °C; see Figure 8 (Ar rotation in $Ar_4M_2Li_2$ is still blocked at this temperature; cf. Figure 5 and Table I). The presence of an additional methyl group in the built-in ligand, which increases the steric bulk considerably, apparently results in stereoselective formation of only one $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Au_2Li_2$ stereoisomer in which all four C_{bridge} atoms have the same configuration, either *S* or *R*.

Furthermore, the observation that in the ^{13}C NMR spectra the chemical shifts for the respective resonances are invariant with temperature (except for Me-N) suggests that introduction of an α-methyl group in the built-in ligand also increases the barrier to rotation of the aryl ring around C_b–C(4) in V. In order to further study the influence of the introduction of an α-Me group $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$ was synthesized.

Stereoisomerism and Aryl Rotation in $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$

According to molecular weight determinations and ^{1}H NMR spectroscopy the $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$ compound has the same structural features as the $(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Cu_4$ cluster.[12] In contrast to the deceptively simple spectra of the latter compound,[12] the ^{1}H and ^{13}C NMR spectra of the C-chiral $(S)\text{-}Ar_4Cu_4$ compound provide valuable information concerning Cu–N coordination and the stereochemistry of the Cu_4 aggregate.

The C_{bridge} atoms in the Cu_4 aggregate are prochiral because they bridge two Cu atoms which have the same trigonal coordination geometry. Accordingly, the $(S)\text{-}ArCu_2$ units in $(S)\text{-}Ar_4Cu_4$, unlike the (S)-ArAuLi units in $(S)\text{-}Ar_4Au_2Li_2$, are not diastereomeric. However, the intriguing point is that the formation of Cu–N coordination bonds in the geometric isomer having the butterfly Cu_4 core shown for $(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Cu_4$[12] can be effected in two ways, i.e., clockwise or counterclockwise.[34] The resulting helicity in combination with the distinct chirality at the benzylic C atoms then gives rise to two stereoisomers denoted $4(S)_C\alpha_{Cu_4}$ and $4(S)_C\beta_{Cu_4}$ which will have different spectra.

The ^{1}H and ^{13}C NMR spectra of $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4]_4Cu_4$ are shown in Figure 9 and Table II. The ^{13}C NMR spectrum at −63 °C reveals two resonance patterns consisting of two singlets for C_b, C(2) or -(6), N-C(H), α-C(H_3), and two singlets and a not yet decoalesced resonance for N-C(H_3). The ^{1}H NMR spectrum at −60 °C likewise reveals two patterns. These spectra establish that Cu–N coordination blocks inversion at the N atom because the singlet resonance observed for the NMe protons at room temperature

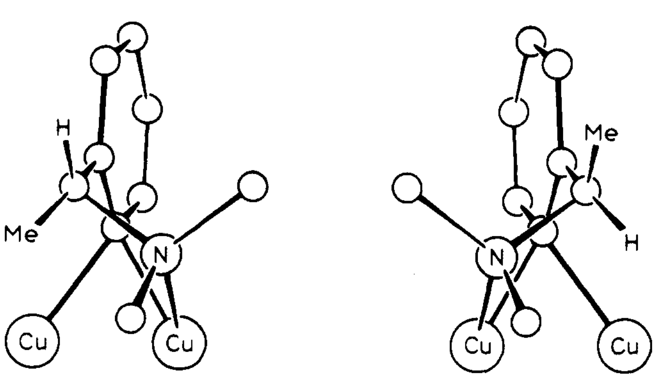

Figure 10. Puckering of the five-membered chelate ring in each of the stereoisomers $4S_C\alpha_{Cu_4}$ and $4S_C\beta_{Cu_4}$.

has been decoalesced into two sets of two singlets at −60 °C. The fact that the whole pattern is doubled at low temperature indicates that indeed the Cu_4 aggregate has frozen out in two stereoisomeric forms. At ambient temperature these two patterns coalesce into one pattern of sharp resonances both in the ^1H and ^{13}C NMR spectra. The coalescence of the NMe protons points out that Cu–N dissociation followed by inversion at N and concomitant C–N rotation has become a fast process on the NMR time scale. The coalescence of the α-C, C(2) or -(6), and C_{bridge} resonances in the ^{13}C NMR spectrum confirms that at ambient temperature the helicity as a chiral element is lost as a result of Cu–N bond dissociation (shift of δ(Me)C–N) in the (*S*)-Ar_4Cu_4 aggregates.

The above-discussed dynamic NMR patterns, however, do not justify further conclusions pertinent to the occurrence of processes such as rotation of the aryl ring around C_b–C(4) or the occurrence of inter- or intraaggregate exchange of the aryl groups. That indeed great care must be taken is shown by the fact that we established by using mass spectrometry the occurrence of interaggregate exchange in solutions containing Ar_4Cu_4 and $(5\text{-}MeAr)_4Cu_4$.[12]

It is worthy of note that the spectra at about −60 °C show quite distinct chemical shift differences for the nuclei in each of the two stereoisomers $4S_C\alpha_{Cu_4}$ and $4S_C\beta_{Cu_4}$. These differences are most probably due to the puckering of the five-membered chelate rings. Depending on the helicity in a distinct Cu_4 aggregate the α-Me group of the built-in ligand is close to or pointing away from the Cu_4 core (see Figure 10 showing one (*S*)-$ArCu_2$ unit).

In the above-discussed process for (*S*)-Ar_4Cu_4 the occurrence of Cu–N bond interaction plays a crucial role. Helicity in a polynuclear aggregate as a result of metal–built-in ligand bond formation may also provide an explanation for the dynamic NMR resonances observed for $(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Li_4$[28,35] (see Figure 11). The ^1H NMR spectrum at 25 °C points out that the CH_2 protons as well as the NMe groups are diastereotopic. The latter conclusion is confirmed by the observation in the ^{13}C NMR spectrum of two singlets for the (methyl-N)C atoms; see Table II. In both the ^1H and ^{13}C NMR spectra only one resonance pattern (cf., e.g., one singlet resonance for α-C) is observed. This is in accord with the fact that the Li_4 aggregates having α or β helicity are indistinguishable by NMR because $(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Li_4$, contrary to (*S*)-$Ar_4Cu_4$, contains a prochiral built-in ligand.

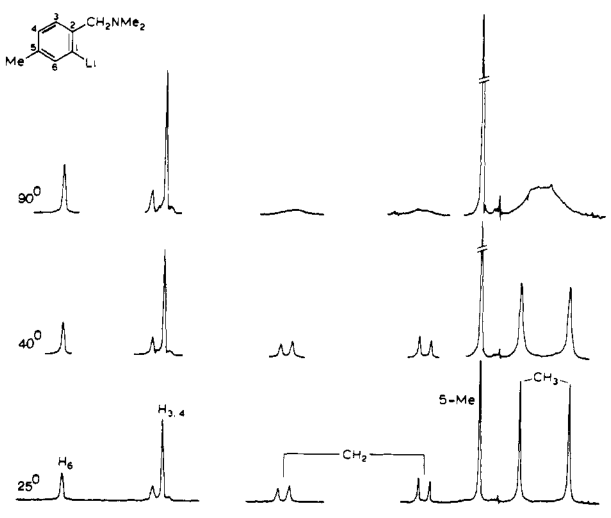

Figure 11. ^1H NMR spectrum (δ ppm) of tetranuclear 5-methyl-2-(dimethylamino)methylphenyllithium in benzene-d_6 at different temperatures.

The spectra in Figure 11 show that the NMe singlets do not coalesce below 90 °C while the AB pattern of the CH_2 protons starts to broaden at this temperature. This high coalescence temperature as compared with the coalescence temperature of −20 °C for the NMe resonances in (*S*)-Ar_4Cu_4 indicates that the Li–N bond in $5\text{-}MeAr_4Li_4$ is stronger than the Cu–N bond in (*S*)-Ar_4Cu_4. It is furthermore interesting to note that the low-field doublet of the AB pattern for $5\text{-}MeAr_4Li_4$ is broadened, whereas the high-field doublet has the same line width as, for example, the methyl signals.[36] A possible origin for this difference is the different position of these protons with respect to the Li_4 core as a result of the puckering in the five-membered chelate ring (compare the situation in Figure 10).

Concluding Remarks

In the foregoing discussion we have seen that the bulkiness of the ortho substituent in the aryl group present in arylmetal-1B clusters has great influence on the barrier to rotation of 3c-2e bonded Ar groups (cf. (*S*)-$Ar_4Au_2Li_2$). The presence of a heteroatom in the ortho substituent, which can form a coordination bond to the bridged metal (e.g., Figure 3B), further contributes to this barrier depending on the strength of the metal–heteroatom bond. Rotation depends in this case on metal–heteroatom bond dissociation. Anchoring of the aryl ring in the perpendicular position by metal–heteroatom coordination also occurs in the hexanuclear clusters $(2\text{-}Me_2NC_6H_4)_4M_2M'_4X_2$.[8,24] In these clusters the $2\text{-}Me_2NC_6H_4$ group spans three metal atoms (cf. structures in ref 8). Also in this case the rotation process of the aryl ring around C_b–C(4) is coupled to metal–heteroatom bond dissociation.[37]

In the case of a five-membered chelate ring the puckering of this ring causes the aryl ring to occupy a position almost perpendicular to the metal–metal axis.[38] This means that in addition to the all-bonding σ aryl-to-metals interaction (see Figure 1) also a maximum overlap can exist between the C_b p orbital and the antisymmetric metal orbital combination. Moreover, in this system back-bonding from the metals to the aryl ring can occur. Accordingly, the rotamers having the aryl ring in perpendicular position either as a result of the presence of bulky substituents or of coordinating substituents in the ortho position have high electron density in the M–C region.[6] These considerations at the same time provide a rationale for the high kinetic stability of these ortho-substituted arylmetal-1B clusters.[39] The stability decreases in the series $2\text{-}Me_2NHZCH_2$ (Z = H or Me) ≈ $2\text{-}Me_2CHCH_2C_6H_4$ ≈ $2\text{-}Me_2N$[40] ≈ $2,6\text{-}(MeO)_2$[40] ≈ $2,6\text{-}Me_2$[16] > 2-Me > 4-Me ≈ unsubstituted phenylcopper.

Experimental Section

The compounds described in this paper have been synthesized according to earlier reported procedures.[8,12,13,21,23,28] Preparation of solutions for ^1H and ^{13}C NMR spectroscopy was carried out under dry, oxygen-free nitrogen. Solvents were purified, dried, and distilled under nitrogen before use. The NMR tubes were sealed under nitrogen.

^{1}H NMR spectra were recorded on a Varian Associates HA-100 NMR spectrometer and the ^{13}C NMR spectra on a Varian Associates XL-100/15 FT spectrometer.

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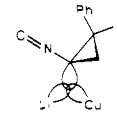
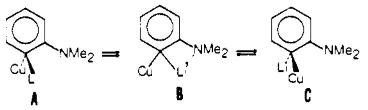
References and Notes

(1) Part 30 in the series of "Group 1B Organometallic Chemistry". For part 29 see ref 2. The results presented in this paper were discussed by G. van Koten at the XVIIth ICCC Conference in Hamburg[3] and at the 1st International Symposium on Homogeneous Catalysis in Corpus Christi, Texas.[4,5] (b) University of Amsterdam. (c) Institute for Organic Chemistry TNO.
(2) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **174,** 367 (1979).
(3) G. van Koten and J. G. Noltes, Abstracts, XVIIth International Conference on Coordination Chemistry, Hamburg, 1976, p 236.
(4) G. van Koten and J. G. Noltes, Abstracts, 1st International Symposium on Homogeneous Catalysis, Corpus Christi, Texas, 1978, p 110.
(5) G. van Koten and J. G. Noltes, *Int. Symp. Homogeneous Catal., Proc., 1st*, **3,** 953 (1979).
(6) G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Org. Chem.*, **42,** 2047 (1977).
(7) G. van Koten, R. W. M. ten Hoedt, and J. G. Noltes, *J. Org. Chem.*, **42**, 2705 (1977).
(8) G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *Inorg. Chem.*, **16,** 1782 (1977).
(9) R. W. M. ten Hoedt, J. G. Noltes, and G. van Koten, *J. Chem. Soc., Dalton Trans.*, 1800 (1978).
(10) J. A. J. Jarvis, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 999 (1977).
(11) The occurrence of direct Cu–Cu bonding could be excluded.[12] The Cu–Cu interaction in these clusters can be formulated as assisted Cu–Cu bonding; cf. ref 9 and 12.
(12) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **84,** 129 (1975).
(13) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, W. M. G. F. Pontenagel, J. Kroon, and A. L. Spek, *J. Am. Chem. Soc.*, **100,** 5021 (1978).
(14) T. Clark and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 137 (1978).
(15) A. Baici, A. Camus, and G. Pellizer, *J. Organomet. Chem.*, **26,** 431 (1971).
(16) H. K. Hofstee, J. Boersma, and G. J. M. van der Kerk, *J. Organomet. Chem.*, **144,** 255 (1978).
(17) Cf. ref 6 (in particular footnote 22) for a discussion of the aggregation state of 2- and 4-tolylcopper compounds as well as of the bonding in these polynuclear species.
(18) Previously reported (*S*)-1-isocyano-2,2-diphenylcyclopropylcopper reagent is an example of a compound in which copper is directly attached to an sp^3 hybridized, chiral, C atom.[19] Although the structure of this reagent is unknown, bonding of the cyclopropyl anion as shown in the figure can be anticipated. The configurational stability of the cyclopropyl anion was attributed to the strain in the ring system which enlarges the energy barrier to the planar intermediate or transition state and thus lowers the rate of inversion.[20] In the aryl anions 2-$Me_2NCH_2C_6H_4$ C_{bridge} is prochiral but becomes chiral by bridging two different metal atoms (see Figure 3).



(19) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, **97,** 5930 (1975).
(20) M. P. Periasamy and H. M. Walborsky, *J. Am. Chem. Soc.*, **99,** 2631 (1977).
(21) G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 940 (1972).
(22) A. J. Leusink, G. van Koten, J. W. Marsman, and J. G. Noltes, *J. Organomet. Chem.*, **55,** 419 (1973).
(23) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **82**, C53 (1974).
(24) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **102**, 551 (1975).
(25) A. J. Leusink, G. van Koten, and J. G. Noltes, *J. Organomet. Chem.*, **56,** 379 (1973).
(26) Unambiguous specification of the configuration at the bridging C atom of 3c–2e bonded aryl groups as *S* or *R* is possible in the following way. The metal atoms bridged by the aryl ring are arranged with the atom with the lowest atomic number behind the plane of the aryl ring. In the three-dimensional model the atoms connected to the bridging C atom are arranged in a sequence of decreasing priority. If the bridged metal atoms have the same atomic number the atom with the highest coordination number is given the highest priority.
(27) This possibility for separate detection of metal–N dissociation and inversion of configuration at the chiral center is fully analogous to that described for the chiral triorganotin halides containing the CH_2NMe_2 group as a built-in ligand.[13]
(28) See ref 2. The angles at the bridging C atoms are acute (cf. ref 12). As a result of linear hybridization at M the C_bMC_b' angle formed by the interatomic vectors is smaller than 180° (cf. ref 8, figure in footnote 10).
(29) In the all-corner situation for the $Ar_4Ag_2Li_2$ cluster two aryl groups are bound to lithium and the other two aryl groups to silver.
(30) In spite of the fact that both copper isotopes ^{63}Cu and ^{65}Cu (total natural abundance of 100%) have a spin moment of $^3/_2$, no ^{13}C–^{63,65}Cu couplings were observed. This may be due to the large quadrupole moment of Cu which interferes with the electric field gradient produced by the surrounding electric charges at the position of the Cu nucleus.
(31) C. H. Bushweller, C. Y. Wang, J. Reny, and M. Z. Lourandos, *J. Am. Chem. Soc.*, **99,** 3938 (1977).
(32) Also the 270-MHz proton spectrum (by M. Nilsson and co-workers, University of Goteborg, Sweden) of V in toluene-d_8 at 35 °C revealed only one resonance pattern.
(33) The possibility that the chemical shift differences between the $S_{C_b}S_C$ and $R_{C_b}S_C$ units are too small to be detected cannot be ruled out (cf., however, the detection of diastereomeric units in $[(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4]_4Cu_4$; see next section).
(34) Note that the aryl groups are alternating above and below the butterfly type Cu_4 core, which has C_2 overall symmetry.[12]
(35) Recently, F. T. Oakes and J. F. Sebastian, *J. Organomet. Chem.*, **159,** 363 (1978), reported the ^{1}H and ^{13}C NMR spectra of 2-$Me_2NCH_2C_6H_4Li$ in THF. We have found (cf. ref 12) that substitution of 2-$Me_2NCH_2C_6H_4Li$ at the 5 position results in benzene- and ether-soluble aryllithium compounds. Addition of ether to a benzene solution of 5-Me-2-$Me_2NCH_2C_6H_3Li$ tetramer[21] results in coalescence of the diastereotopic NMe and benzylic proton resonance patterns (cf. ref 28). Replacement of Li–N by Li–ether coordination bonds removes the origin of the chirality in the Ar_4Li_4 aggregates. The $\delta(NMe_2)$ values of 5-Me-2-$Me_2NCH_2C_6H_3Li$ in THF are found very near the NMe value in the nonmetalated $Me_2NCH_2C_6H_4X$ compounds.
(36) Proton decoupling experiments (irradiation at H(6), H(3), and the position of the other benzylic proton and of the methyl protons) revealed that the broadening is not due to coupling with one of the other protons.
(37) Cf. Figure 3 in ref 24, which shows the ^{1}H NMR spectrum of (2-$Me_2NC_6H_4)_4Cu_6Br_2$. Coalescence does not occur below 60 °C.
(38) In contrast the interaction of built-in ligands which are directly attached to the aryl ring (i.e., in 2-$MeOC_6H_4$ or 2-$Me_2NC_6H_4$) with one of the bridged metals is only possible if the aryl ring resides in the plane through the 3c–2e C_{Ar}MLi bond (situation B). In this case the barrier to rotation of the aryl nucleus around C_b–C(4) is lowered. It is even possible that situation B represents a stable intermediate in which C_b, however, is no longer a chiral center. In $(2\text{-}Me_2NC_6H_4)_4M_2Li_2$ (M = Cu, Au) the methyl-N signals are isochronous.[26] F. A. Cotton and M. Millar, *J. Am. Chem. Soc.*, **99**, 7886 (1977), established $V_2[2,6(MeO)_2C_6H_3]_2$ as the first example of B. When the 2-$Me_2NC_6H_4$ group bridges three metal atoms as in $(2\text{-}Me_2NC_6H_4)_4M'_2M_4X_2$ situation A is stabilized because the built-in ligand now coordinates to a third metal atom (see ref 8). In this case C_b is a center of chirality.



(39) 8-Phenylnaphthylcopper as well as 2-$(Me_2CHCH_2)C_6H_4Cu$, in which the ortho substituents are extremely bulky but lack coordinating substituents, do not decompose below 180 °C.[26]
(40) G. van Koten, A. J. Leusink, and J. G. Noltes, *J. Organomet. Chem.*, **85,** 105 (1975).