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Preliminary communication

INTRAMOLECULAR DYNAMICS OF 3*c*—2*e* BONDED ARYL GROUPS IN POLYNUCLEAR ARYL-COPPER, -SILVER AND -GOLD DERIVATIVES

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Summary

Dynamic ^{1}H and ^{13}C NMR studies reveal that the prochiral methylene group in 2-(Me_2NCH_2)C_6H_4-metal compounds $R_4M_2Li_2$ (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 3*c*—2*e* bonded aryl groups around the C(1)· · ·C(4) axis has been unambiguously established for the first time. Chiral labelling of the 3*c*—2*e* bonded group provides information concerning the stereochemistry of the $R_4M_2Li_2$ cluster.

Selective C—C coupling processes taking place on a cluster surface have to our knowledge only been established for polynuclear organocopper compounds [1]. X-ray structure determinations showed that in the organocopper clusters the organic groups are bonded via multicenter carbon—metal interactions [1,2]. Sofar little is known concerning the intramolecular dynamics of these organic groups in solution. The understanding of this aspect is important for the elucidation of C—C coupling processes taking place on cluster surfaces.

We report here NMR-spectroscopic data which provide unambiguous proof that the 3*c*—2*e* bonded aryl groups present in arylmetal (IB) clusters rotate around the C(1)· · ·C(4) axis. Recently reported evidence for the occurrence of such rotation in 2-tolylcopper [3] is ambiguous in that a process involving inter- or intra-aggregate exchange of 2-tolyl groups, a process well-established for tetranuclear arylcopper compounds [2], cannot be excluded.

The compounds studied are of the type (2-$Me_2NCHZC_6H_4$)$_4M_{4-n}Li_n$ (Z = H or Me; n = 0, 2 or 4; M = Cu, Ag or Au) and were obtained by procedures reported elsewhere [4—7]. Their structures consist of a $M_{4-n}Li_n$ core to which the 2-$Me_2NCHZC_6H_4$ groups are bonded via 3*c*—2*e* bonds. X-ray analysis showed

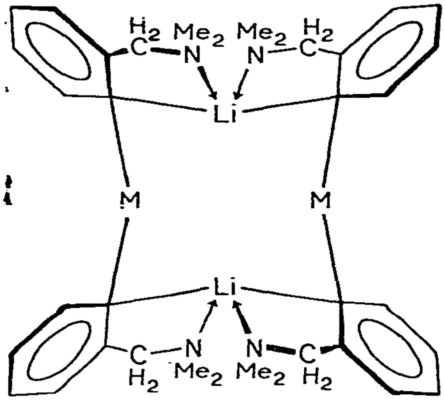


Fig. 1. Schematic structure of the $(2\text{-}Me_2NCH_2C_6H_4)_4M_2Li_2$ (M = Cu, Ag or Au) compounds.

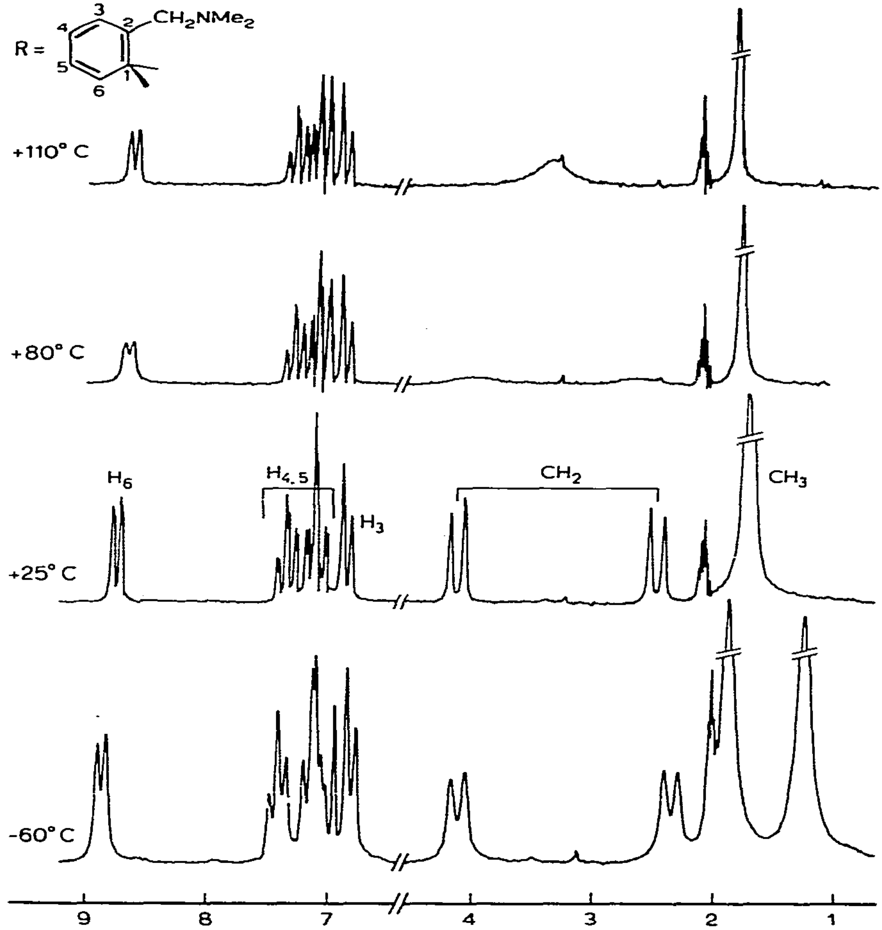
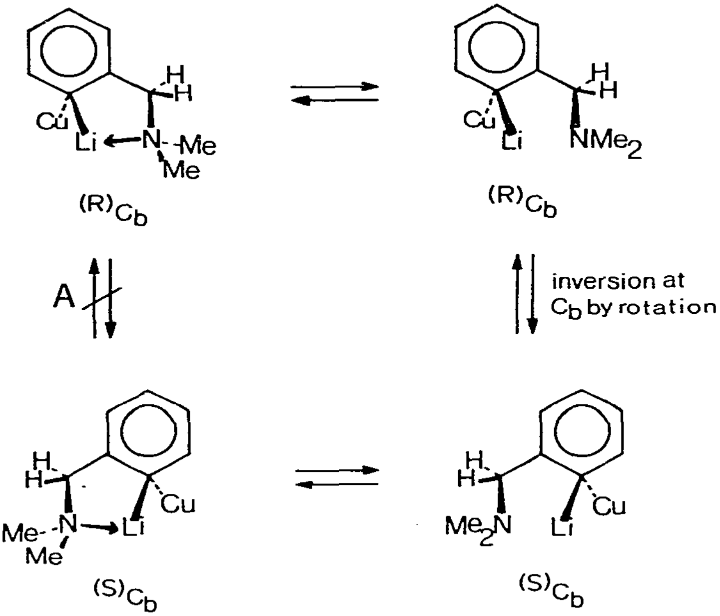


Fig. 2. ^{1}H NMR spectra (δ, ppm) of $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_2Li_2$ in toluene-d_8 at different temperatures.

that each of the Cu atoms in $(5\text{-Me-2-Me}_2NCH_2C_6H_3)_4Cu_4$ have trigonal coordination geometry resulting in C_2 symmetry for the aggregate, i.e. a folded Cu_4 core [2]. The $R_4M_2Li_2$ compounds posses a *trans*-M_2Li_2 core with two-coordinate M and four-coordinate Li atoms, see Fig. 1.

Inter- or intra-aggregate exchange between or in these clusters must be slow on the NMR time scale, because in the case of $R_4Ag_2Li_2$ both the $J(^{107,109}Ag—^{13}C(1))$ (118.3 and 136.0 Hz respectively) and the $J(^7Li—^{13}C(1))$ (7.2 Hz) [5] remain unaltered over the temperature range studied. This shows that the 3*c*—2*e* RAgLi bond remains intact on the NMR timescale [5]. Accordingly, the ^1H DNMR patterns shown for $R_4Cu_2Li_2$ in Fig. 2 must involve intramolecular dynamic processes which leave the 3*c*—2*e* RCuLi bond unaffected (cf. Scheme 1).



SCHEME 1. Scheme showing the Li—N dissociation/aryl rotation process accounting for the spectra in Fig. 2.

In the $R_4M_2Li_2$ clusters each of the bridging C(1) atoms represents a center of chirality (R is dissymetrically substituted; bridges unlike metal atoms). Rotation of the aryl ring around the C(1)· · ·C(4) axis will cause a continuous inversion of configuration at C(1). It must be noted that overlap in the lowest MO for the 3*c*—2*e* bond is equal in each of the rotamers because the symmetry axis of this MO coincides with the C(1)· · ·C(4) axis [2]. Rotamers $(S)_{C_b}$ and $(R)_{C_b}$ in Scheme 1 represent the enantiomeric pair for one rotamer conformation in the limiting situation. In these RMLi units inversion of configuration at C(1) as a result of rotation can be detected by NMR spectroscopy, because the CH_2NMe_2 ligand contains a prochiral CH_2 group. Moreover, the occurrence of Li—N coordination can be detected, because in the coordinated situation the Me_2N group is likewise a stable prochiral assembly.

The ^1H NMR spectra show that the AB pattern for the NCH_2 protons and the two singlets for the NMe protons coalesce with different rates, while the coalesced NMe_2 singlet is shifted downfield from the averaged positions of the two NMe singlets at low temperatures. This excludes route A in Scheme 1 and points to the occurrence of two different processes, i.e. Li—N dissociation and aryl rotation. In the rotamers with NMe_2 coordinated to Li both the NCH_2 protons and the NMe groups are diastereotopic. At higher temperatures the two NMe resonances become isochronous. This can only be explained by a process involving N—Li bond dissociation, inversion at N and concomitant C—N bond rotation followed by coordination*.

The AB pattern for the diastereotopic NCH_2 protons is still present up to 90°C. This indicates that inversion of configuration at C(1) does not occur on the NMR time scale, which shows that rotation of the aryl group has become the rate-determining step. At 95°C the NCH_2 protons have become isochronous as a result of rapid rotation of the aryl groups around the C(1)· · ·C(4) axis.

The barrier to rotation created by the *ortho*-substituent can be further increased by replacement of one of the benzylic protons by a methyl group**. Interestingly, this substitution introduces a second center of chirality of which the configuration cannot invert. Combination of the two chiral centers results in two diastereomeric forms $(S)_{C_b}(S)_C$ and $(S)_{C_b}(R)_C$ (starting from (*S*)-2-$Me_2NCHMeC_6H_4$) for each of the RMLi units which will display different NMR spectra. This then in principle enables information to be obtained about the stereochemistry of the R_4M_2Li cluster. The NMR spectrum of [(*S*)-2-$Me_2NCHMeC_6H_4]_4Au_2Li_2$ shows only one set of signals, revealing that all four C(1) atoms have the same configuration: either *S* or *R*.

Furthermore, by using this principle of chiral labelling of the 3c—2*e* bonded aryl group we have shown that in [(*S*)-2-$Me_2NCHMeC_6H_4]_4Cu_4$ Cu—N coordination occurs in solution at low temperatures (–65°C). However, this Cu—N coordination is weak as compared with the Li—N coordination [9] in (5-Me-2-$Me_2NCH_2C_6H_3)_4Li_4$ which is still inert on the NMR timescale in benzene at 90°C.

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*Pyramidal inversion at N as well as C—N bond rotation are low energy processes with barrier amounting to 6 kcal/mol [8]. Consequently, the coupled inversion and C—N bond rotation processes are fast over the whole temperature range studied.

**The presence of bulky substituents in the *ortho* position stabilizes rotamers having the aryl ring in almost perpendicular position with respect to the metal—metal axis. In this situation additional bonding between the p_z-orbital at C(1) and the antisymmetric metal orbital combination can occur. This further stabilizes the CMM′ bond because of enhancement of the electron density in the M—C region. This is reflected in the kinetic stability of the *ortho*-substituted arylmetal(IB) clusters which decreases with decreasing bulkiness in the series: 2-$Me_2NCHZCH_2$ (Z = H [2] or Me [7]) ≈ 2-$Me_2CHCH_2C_6H_4$ [9] ≈ 2-Me_2N [2] ≈ 2,6-$(MeO)_2$ [10] ≈ 2,6-Me_2 [3] > 2-Me [1] > 4-Me [1] ≈ *unsubstituted phenylcopper.*

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