of the rate determining nucleophilic attack on an ion–molecule pair, formed in a preequilibrium step. Whereas the latter mechanism is the only one operating in the reaction of the *p*-methoxybenzyl derivative **1** at all pressures investigated, the benzyl derivative **2** reacts predominantly by this path when the pressure is low but by the concerted mechanism when it is high. From the difference $\Delta(\ln k^0)$, the ratio of rate constants at zero pressure is estimated to be 2–2.5; in other words, the ion–molecule pair mechanism contributes 65–70% of the reaction under ambient conditions, and the simple S_N2 reaction accounts for the rest. We point out that the difference in activation volume between these two competing paths, $\Delta\Delta V^{\ddagger}$ is simply the difference in partial volume between the two isomeric transition states. Its huge value of ca. 40 cm^3/mol is comparable to the reaction volume of the Diels–Alder process—which also relates a pair of states differing by two chemical bonds!

Involvement of the perchlorate and tetrafluoroborate counterions cannot be invoked to explain the minimum. While such involvement has at times bedeviled kinetic high-pressure investigations of electrolytes in media of low polarity,[9] the low (UV) concentrations used here and the demonstrated independence of the rates on the nature of these ions[10] rule out any such complication here.

Although $\Delta V^{\ddagger}$ had not previously been used as evidence for cation–molecule pairs, one of us has published such evidence implicating anion–molecule pair intermediates.[11] This evidence was subsequently confirmed by means of demonstrations of internal return[12] and of retained configuration.[13] The only precedent for the pair proposed here is the pyridine–trityl cation pair suggested by Streitwieser[14] to explain a special feature of that reaction published by Hughes and Ingold.[15] A closely related development is the intervention of the phenyl cation–nitrogen molecule pair in the dediazonation of benzenediazonium cations reported by Zollinger.[16] Our proposal is reminiscent of that of Sneen,[17] who emphasized that bimolecular nucleophilic displacements of secondary alkyl tosylates and similar *neutral* substrates could occur at the intimate *ion* pair stage of the Winstein solvolysis scheme.[18] That suggestion gave rise to much controversy, and there is no agreement that a genuine case has been recognized; indeed, the *modest*, negative $\Delta V^{\ddagger}$ values observed in *these* reactions are in better accord with the classical S_N2 model than with prior *ionization*, which is known to be much more powerfully enhanced by pressure ($\Delta V^{\ddagger}$ *large* and negative).

The shape of the ln *k* vs. *p* curve in the reaction of **2** is a unique example of the traditionally difficult problem of deciphering a reaction subject to competing mechanisms obeying the same observed rate law;[19] one can then obviously not make either pathway dominant by manipulating concentrations. One of us pointed out some 15 years ago[20] that, in those instances in which, first, the two pathways have rates that are not too dissimilar and, second, the faster one possesses a positive activation volume and the slower one is characterized by a negative value, the effect of pressure on the observed rate constant will reveal this kind of duplicity by exposing a minimum. No genuine examples of such plots had been reported to date.[21]

In summary, we have found a unique response of a rate constant to pressure variation. Our results demonstrate that both the classical S_N2 and the ion–molecule pair mechanisms can occur in the title reactions. They compete in one instance, and the extraordinarily large difference in volume (ca. 40 cm^3/mol) between the two transition states leaves no doubt about the nature of their structural difference.

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Solid-State Structure of [$Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$]: A Model for the Reactive Structure of Organocuprates

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So far the cuprates, argentates, and aurates of the formula $M_2Li_2(C_6H_4X)_4(OEt_2)_n$ (X = 4-Me, $n = 2$;[1a] X = 2-Me_2NCH_2, $n = 0$;[1b] see Figure 1) are the only metal 1B–lithium species for which the structures *in solution* could be established by molecular weight measurements as well as ^{1}H, ^{13}C, ^{6}Li, and ^{7}Li NMR.[1,2] Observation of a $^{1}J(^{13}C(1)\text{–}^{7}Li)$ for these compounds and a $^{1}J(^{107,109}Ag\text{–}^{13}C(1))$ for $Ag_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$ (**1b**) [1] established that (i) the metal 1B and the lithium atoms are part of the same cluster[3] and (ii) each of the aryl groups is three center-two electron bonded to a metal 1B–lithium atom pair. This information concerning the structure *in solution* is of prime importance for a better understanding of the mechanistic aspects of organocuprate reagents. The preferential coordination in **1** and **2**[3] of the N- and O-donor ligands to lithium rather than to the 1B metal gives credence to the belief that the lithium atoms are the anchoring sites of the α,β-unsaturated ketones (via O) in the conjugate addition reaction using organocuprates.[5]

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(2) The ^{6}Li and ^{7}Li NMR spectra of $Ag_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$ in benzene-d_6 showed a triplet with a 1/2/1 intensity ratio (δ Li -0.10, $LiCl/D_2O$ external reference) due to $^{2}J(^{6}Li\text{–}^{107,109}Ag) = -1.46$, and $^{2}J(^{7}Li\text{–}^{107,109}Ag) = 3.91$ Hz. Brevard, C.; Jastrzebski, J. T. B. H.; van Koten, G., unpuslished results.

(3) In more basic ethers (i.e., THF) or in the presence of the powerful terdentate ligand pentamethyldiethylenetriamine the neutral CuLi clusters are transformed into ionic species in which the Li and Cu atoms are part of different units, i.e., $Ph_6Cu_5Li\cdot4THF$ consists of a homonuclear anionic $Ph_6Cu_5^-$ cluster and $Li(THF)_4^+$ cations.[4]

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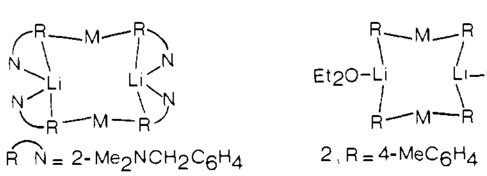

Figure 1. Schematic structures of some cuprates (M = Cu; **1a**, **2a**), argentates (M = Ag; **1b**, **2b**) and aurates (M = Au; **1c**, **2c**) in solution as based on ^1H, ^{13}C, $^{107,109}Ag$, and $^{6,7}Li$ NMR data.

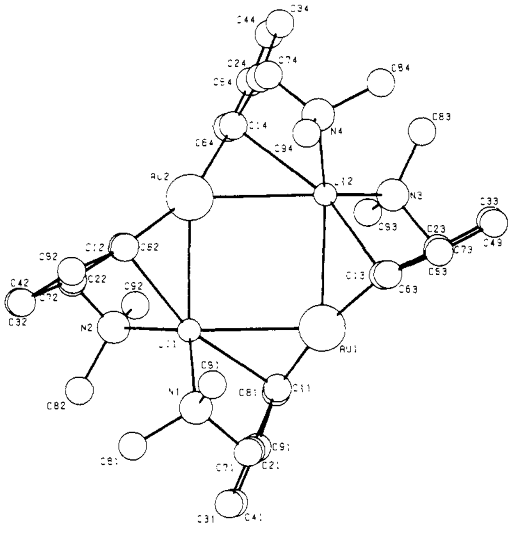

Figure 2. Molecular geometry of $[Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$. Important, selected, intramolecular distances (Å) and angles (°): Au(1)-Li(1) 2.86 (3), Au(1)-Li(2) 2.90 (3), C(11)-Au(1) 2.06 (2), C(13)-Au(1) 2.06 (2), C(11)-Li (1) 2.58 (2), C(12)-Li(1) 2.45 (3), N(1)-Li(1) 2.24 (3), N(2)-Li(1) 2.21 (3), Li(1)-Au(1)-Li(2) 92 (1), Au(1)-Li(1)-Au(2) 87 (1), C(11)-Au(1)-C(13) 167 (1), C(11)-Li(1)-C(12) 165 (2), N(1)-Li(1)-N(2) 125 (1).

We now report the structure in the solid state of $[Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$,[6] which is the first example of a neutral aryl metal 1B lithium compound containing both the metal 1B and the lithium atoms in one cluster core. A unique feature of the structure is the presence of asymmetrically bridging aryl groups.

The molecular geometry of **1c** is shown in Figure 2 together with some important bond distances and angles. Figure 2 illustrates clearly that the structure consists of two ArAuAr anionic units and two cationic N_2Li sites. The latter units form together a unique (virtually planar) $Au_2Li_2C(ipso)_4$ entity that has a square planar Au_2Li_2 arrangement with LiAuLi and AuLiAu angles close to 90° and AuLi distances of 2.87 Å (mean). The orientation of each of the aryl groups suggests that they are primarily bonded via C(ipso) to Au by a two-electron, two-center bond. The Au-C bond lengths (2.06 Å mean) are comparable to those reported for the $Au(C_6F_5)_2^-$ anion.[8] Another striking similarity with the latter anion is the almost linear arrangement of the CAuC units (bond angles 166° (mean), see Figure 2) as well as the near coplanarity of the two aryl nuclei, which are bonded to the same Au atom. The four neutral N-donor-containing substituents coordinate exclusively to the Li atoms, as expected,[1] with Li-N bond lengths of 2.24 Å (mean) (cf.[9] Li-N of 2.15 Å (mean) in $Li_4(C_6H_4CH_2NMe_2\text{-}2)_4$). Furthermore, the N-Li-N angle of 125° (mean) is much larger than expected for three- or four-coordinate Li cations. Finally, the Li atoms seem to form a special[10] arrangement with C(ortho) (2.75 Å mean), Au(1) (2.88 Å mean), and C(ipso) (2.46 Å mean). In view of the latter arrangement the occurrence of an η-type interaction between this part of the $ArAuAr^-$ moiety and N_2Li^+ cation [10a] cannot be excluded although the fact that the aryl nuclei are geometrically undisturbed (see Figure 2; all aryl- and benzylic-C atoms are in one plane) seems to oppose this possiblity.[11]

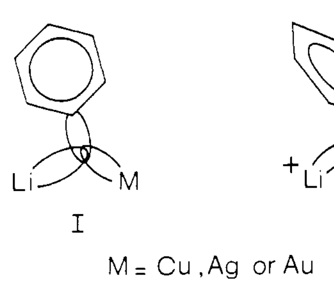

Figure 3.

The NMR results of $M_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$ (**1**) indicate that in solution the carbon sp^2 lone pair of the aryl anion in the lithium-aryl-metal 1B bridge interacts with both lithium and the 1B metal (see I, Figure 3).[1] It must be anticipated, however, that because of the different orbital size and energy of the 1B metals the interaction of the sp^2-C aryl anion with the metal 1B center becomes increasingly predominant going down the series Cu^I to Ag^I to Au^I. Accordingly, the lithium-aryl-metal 1B bridge in **1a**, **1b**, and **1c** is expected to become increasingly asymmetric ultimately leading to the two-center, two-electron bonding of **1c** in the solid reported here. In this structure the aryl sp^2 lone pairs are almost exclusively bonded to the Au atoms (see II, Figure 3) and the lithium sites are the electropositive centers to which the heteroatoms are coordinated. This makes **1c** an interesting model for the reactive transient organocuprate-substrate species that are postulated[12] to be formed in reactions of simple organocuprates (e.g., $Cu_2Li_2Me_4$) with organic substrates (e.g., α,β-unsaturated ketones). This study reveals that structural transformations from I to II,[13] which also enhance the nucleophilicity of the copper center, are feasible with retention of the square-planar Li_2M_2 structure.

Acknowledgment. Prof. K. Vrieze is thanked for his stimulating interest.

Supplementary Material Available: Table of atomic coordinates, anisotropic thermal parameters, observed and calculated structure factors, and bond distances (Å) and bond angles (15 pages). Ordering information is given on any current masthead page.

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(6) Crystals of the title compound, $Au_2Li_2C_{36}H_{48}N_4$, are monoclinic, space group $P2_1/c$, with four molecules in a unit cell of dimensions a = 17.34 (2) Å, b = 13.91 (1) Å, c = 15.21 (1) Å, and β = 93.25 (4)°. 2494 reflections with intensities above the $2.5\sigma(I)$ level were measured on a NONIUS CAD4 diffractometer using graphite monochromated Mo Kα radiation. The Au positions were derived from a Patterson synthesis and Li, C, and N were found from a subsequent ΔF synthesis. After isotropic block-diagonal least-squares refinement an emprical absorption correction (DIFABS)[7] was applied (crystal dimensions 0.55 × 0.25 × 0.3 mm; μ = 80.1 cm^{-1}). Continued anisotropic refinement converged to R = 0.034. In a final ΔF synthesis the residual effects near Au were about 0.9 e-/Å^3. The anomalous dispersion of Au was taken into account, and a weighting scheme $\omega = 1/(20 + F_o + 0.005F_o^2)$ was applied.

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(10) (a) This Li---C distance is far longer (2.50 Å mean) than expected, not only for either electron-deficient or -precise aryl-Li bonds (i.e. 2.22 Å)[10] but also for an interaction of an empty Li p orbital with the aryl p_z orbitals (cf. indenyllithium TMEDA, Li-C 2.25 Å (mean)).[10b] (b) Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 757.

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(13) Similar transformations have been established for, for example, (i) mesitylcopper, which reacts with dppe to give $[CuAr_2]^-$ anions and $[Cu(dppe)_2]^+$ cations,[14] (ii) $Au_2Cu_4X_2(C_6H_4NMe_2\text{-}2)_4$, which based on ^{197}Au Mössbauer spectra has been formulated as $[Ar_2Au^-Cu_4X_2^{2+}AuAr_2^-]$[15] and (iii) $Cu_2Li_2(C_6H_4Me\text{-}4)_4(TMEDA)_2$, which may have an ion pair structure.[1a]

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