

enediolate formation and isomerization proceed by separate pathways. Common intermediates and facile reversible interconversion of intermediates seem unlikely. Since rotation about the C-C single bond in intermediate E would allow the formation of *both* cis and trans enediolate ligands, the alternative intermediate at this stage of the reaction, F, is an attractive candidate in the enediolate formation sequence. The multiple coordination of the OCCH₂O ligand in F might direct the hydrogen migration step to the cis geometry via a species such as H. Once a coordinating base such as TPPO or THF is added, reversible access to such cis-directing species may be prohibited.

The concentration-dependent isomerization of the cis enediolate to the trans enediolate, observed with both TPPO and THF adducts, is more difficult to explain. The isomerization of bridging enediolate ligands has not been previously observed. The closest related system known to isomerize is the cis enolate ligand of (C₅Me₅)₂Zr^{IV}(*cis*-OCH=CHR), formed initially by hydrogenation of a C,O-η²-ketene ligand.⁵⁹ This compound isomerizes to the trans isomer at 80 °C.⁵⁹

One simple mechanism for the room-temperature isomerization observed in our system would be to assume that the cis products, IIIa and IVa, are kinetic products which isomerize to the thermodynamic products IIIb and IVb, e.g., by rotation about the carbon single bond of an intermediate that has a structure like that of E. Formation of such trans-directing intermediates not accessible in the enediolate formation sequence may be possible in the presence of TPPO or THF. However, such a simplified process would not display the observed rate enhancement on

dilution. A more detailed kinetic analysis of this isomerization is necessary before the interesting concentration dependence of this conversion can be explained.

Conclusion

The ability of lanthanide hydride moieties to reduce and couple CO has been demonstrated in this study. This reaction system also has provided the first structural results on a product derived from the reaction of a lanthanide hydride with CO and the first refinable structural data on any enediolate unit derived from CO and a metal hydride. The fact that the cis enediolate unit, initially formed in this reaction, isomerizes to the trans isomer, a previously unobserved transformation in CO/metal hydride chemistry, raises interesting questions regarding the bonding and stability of the enediolate unit in general. Whether such transformations occur and are observable in other CO/metal hydride system or whether this isomerization is unique to lanthanide-based systems is a question deserving further study.

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Registry No. I, 84751-30-4; IIIa, 94800-57-4; IIIa-3toluene, 94800-58-5; IIIb, 94842-40-7; IVa, 94800-59-6; IVb, 94842-41-8.

Supplementary Material Available: Tables of bond distances and angles for toluene molecules, atomic parameters for group atoms, thermal parameters, and observed and calculated structure factor amplitudes (74 pages). Ordering information is given on any current masthead page.

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Preparation and X-ray Structure Determination of [Li₆Br₄(Et₂O)₁₀]²⁺[Ag₃Li₂Ph₆]⁻²: An Unusual Cation Composed of a Solvated "Salt Cluster"

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Abstract: Following an earlier report of ours on the preparation and structure determination of the [Cu₅Ph₆]⁻ cluster, we have extended this chemistry into silver/phenyl complexes. The [Ag₃Li₂Ph₆]⁻ mixed-metal cluster was prepared by treating a cold suspension (0 °C) of AgBr in diethyl ether with a solution of freshly prepared phenyllithium in a 1:3 molar ratio. After removal of half of the solvent, large colorless crystals of the title compound appeared after a few days at -15 °C. [Li₆Br₄(Et₂O)₁₀]²⁺[Ag₃Li₂Ph₆]⁻² crystallizes in the monoclinic space group P2₁/n, with *a* = 16.466 (9) Å, *b* = 29.700 (15) Å, *c* = 12.821 (5) Å, β = 100.18 (4)°, *V* = 6171 (5) Å³, *Z* = 2. The positions of the Ag and Br atoms were determined by direct methods, and the coordinates of the rest of the atoms were determined by standard heavy-atom techniques. Least-squares refinement resulted in a final *R* factor of 0.070 for 3827 reflections with *I* > 3 σ(*I*). The [Ag₃Li₂Ph₆]⁻ cluster closely resembles the [Cu₅Ph₆]⁻ cluster mentioned earlier, having the same basic trigonal-bipyramidal geometry with lithium atoms in axial positions. The [Li₆Br₄(Et₂O)₁₀]²⁺ cation is extremely unusual: it consists of a [Li₆Br₄]²⁺ salt-like core surrounded by a shell of ten ether molecules.

Organocopper complexes have been used in organic synthesis for many years.¹ This interest has been extended to organosilver compounds for its possible use in organic synthesis² as well as its ability to provide some insight into the chemistry of group 11 elements in general. As an extension of our studies on the phenylcopper system,³ phenylsilver complexes have been investigated.

This paper describes the preparation and structure of one such complex, the [Ag₃Li₂Ph₆]⁻ anion.

The susceptibility of the silver-carbon bond to oxidation and hydrolysis has hindered many early attempts at isolating and characterizing arylsilver compounds.⁴ It was only in 1972 that

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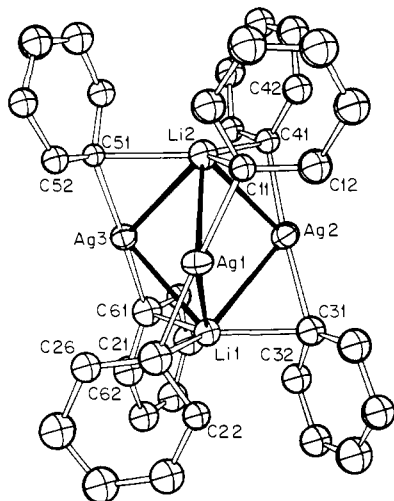


Figure 1. Front view of the $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ anion. The ellipsoids on this and subsequent plots correspond to 80% probability.

pure uncontaminated phenylsilver (subsequently believed to be polymeric⁵) was produced for the first time as a colorless solid.⁶ Phenylsilver itself has not been crystallographically characterized, but the analogous mesitylsilver has recently been shown to be a tetramer.⁷ It should be further mentioned in this introduction that the chemistry of a number of *substituted* aryl silver compounds (usually with OMe, NMe₂, or CH₂NMe₂ groups in ortho positions) has been well-studied:^{8,9} in particular, the first (and only) structural elucidation of an Ag₂Li₂(aryl)₄ cluster in solution by NMR spectroscopy was reported back in 1973.¹⁰ Finally, it should be pointed out that unsubstituted lithium diphenyl argentate has also been prepared recently.⁹

Experimental Section

The $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ anion (with a novel lithium bromide aggregate, $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$, as its counterion) was prepared in the following manner: A solution of freshly prepared phenyllithium (14 mL, 0.87 M in ether, 12.2 mol) was injected to a cold (<0 °C) suspension of silver bromide (0.75 g, 4 mmol) in diethyl ether. The solid silver bromide powder disappeared within a few minutes and a clear light brown solution formed. After removal of about half of the solvent in vacuo and storing the solution at -15 °C, large colorless crystals appeared in a few days.

At room temperature, decomposition of the title compound occurred slowly even under anaerobic conditions. The compound is extremely sensitive to moisture and/or oxygen and decomposes within a few seconds in air. Bright yellow precipitates are formed instantly upon the addition of small amounts of water to the material. This bright yellow decomposition product turns into a gray metallic powder in a few hours.

Because of the (i) air sensitivity, (ii) moisture sensitivity, and (iii) ease of desolvation of the crystals, the Hope-Power crystal-mounting procedure was used.¹¹ A plate-like crystal was used for data collection at -102 °C carried out with Mo K α radiation with an ω -scan mode. The compound crystallizes in the monoclinic space group $P2_1/n$,¹² with $a = 16.466$ (9) Å, $b = 29.700$ (15) Å, $c = 12.821$ (5) Å, and $\beta = 100.18$ (4)°. After data reduction (in which Lorentz, polarization, and absorption corrections

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(12) Space group $P2_1/n$ is an alternative, nonstandard setting of $P2_1/c$ (No. 14) with equivalent positions (x, y, z); ($-x, -y, -z$); ($1/2 + x, 1/2 - y, 1/2 + z$); ($1/2 - x, 1/2 + y, 1/2 - z$).

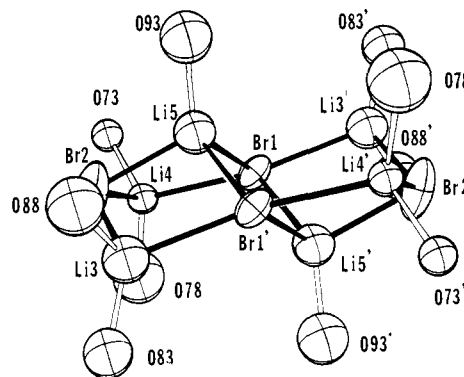


Figure 2. A molecular plot of the $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ cation. The ethyl groups on the ether molecules are omitted for clarity.

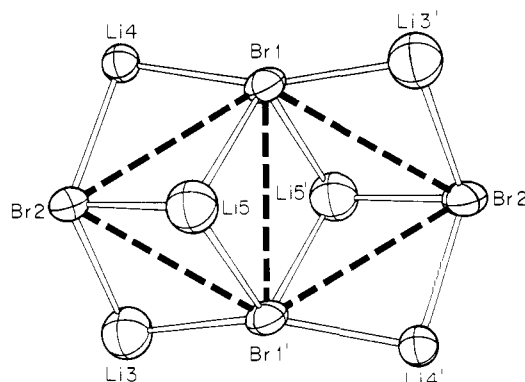


Figure 3. Top view of the central Li_6Br_4 skeleton of the $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ cation.

Table I. Selected Distances and Angles (Averaged) in $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$

$[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ anion		$[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ cation	
(A) Distances (in Å)			
Ag...Ag	3.427 (2)	Br...Br	3.884 (3)
Ag—Li	2.76 (2)	Li—Br	2.58 (2)
Ag—C	2.13 (1)	Li...Li	3.31 (6)
Li...Li	3.83 (4)	Li—O	1.94 (4)
Li—C(ipso)	2.27 (2)		
(B) Angles (in deg)			
Li—Ag—Li	88.2 (9)	Br...Br...Br	119.5 (1), 60.0 (1)
Ag—Li—Ag	76.9 (6)	Br—Li—Br ^a	96 (2)
C—Ag—C	174.7 (7)	Br—Li—Br ^b	100 (1)
C—Li—C	120 (1)	Br—Li—O ^a	112 (2)
Ag—C—Li	78 (1)	Br—Li—O ^b	117 (3)

^aDoubly bridging lithium [i.e., Li(3), Li(4)]. ^bTriply bridging lithium [i.e., Li(5)].

were applied), 3827 unique reflections were retained and used in the subsequent structure analysis. The positions of the silver and bromide atoms were obtained by direct methods.¹³ Subsequent difference-fourier maps revealed all the non-hydrogen atoms. Final full-matrix least-squares refinement^{14,15} (with Ag and Br atoms assigned anisotropic temperature factors) resulted in an R factor of 0.070.

(13) MULTAN: a system of computer programs for the automatic solution of crystal structures for X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368).

(14) Programs used for the least-squares refinement included, initially, DIFSN [a program based on differential synthesis at its method of refinement (McMullan, R. K., private communication)] and, subsequently, CRM (an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology).

(15) The isotropic temperature factor of Li(2) consistently refined to a nonpositive value (~ -0.3). Successful refinement of this atom was achieved by taking into account the possibility of silver contamination at the Li(2) site, resulting in occupancies of 2% silver and 98% lithium at that site. For this partial-occupancy refinement, a temperature factor of 2.8 [equal to that of Li(1)] was assigned to Li(2).

Description and Discussion of the Structure

The structure consists of discrete $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ and $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ ions. A front view of the anion is shown in Figure 1. Figure 2 shows the $[\text{Li}_6\text{Br}_4]^{2+}$ cation (including the ten oxygen atoms from the ether molecules of solvation), and Figure 3 shows the core of the $[\text{Li}_6\text{Br}_4]^{2+}$ cation. A listing of selected distances and angles is given in Table I. A complete set of final atomic coordinates is available as supplementary material (see supplementary material paragraph at end of paper for details).

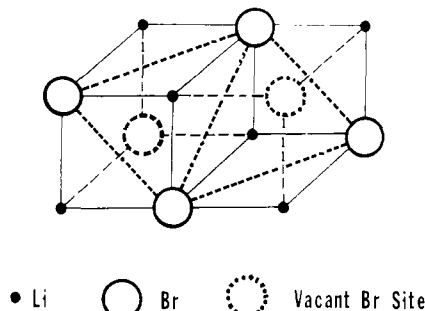
The structure of the $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ anion resembles that of the $[\text{Cu}_5\text{Ph}_6]^-$ anion³ rather closely and is very similar to that of the recently reported $[\text{Cu}_3\text{Li}_2\text{Ph}_6]^-$ anion.¹⁶ It has a trigonal-bipyramidal core made up of lithium atoms at the axial positions of an almost equilateral triangular array of equatorial silver atoms. The two lithium atoms are approximately equidistant from the silver triangle with an average Ag–Li distance of 2.76 (3) Å. This agrees well with the sum (2.79 Å) of the single-bonded covalent radii for Ag (1.45 Å)¹⁷ and for Li (1.34 Å).¹⁸ In contrast, the Ag...Ag separation distances of 3.379 (2)–3.462 (2) Å are considered to be nonbonding.^{19–28}

The six phenyl groups in the anion bridge the six Ag–Li edges of the trigonal bipyramid. The Ag atoms are approximately linearly coordinated [average C–Ag–C angle = 174.7 (7)°], while the two Li atoms are roughly trigonally coordinated (planar within 0.01 Å) with respect to the three bridging C(ipso) atoms. The anion has an approximate D_3 symmetry, with a noncrystallographic C_3 rotation axis passing through the two Li atoms. The diphenylsilver moieties are not parallel to this noncrystallographic threefold rotation axis; instead, they are tilted by an average angle of 26 (3)°.

Another way of visualizing the bonding in the $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ anion is to consider it as an aggregate of three linear $[\text{AgPh}_2]^-$ moieties held together loosely by two Li^+ cations. This phenomenon was noticed very recently by van Koten et al. in a Au/Li/aryl complex,²⁹ in which two $[\text{Au}(\text{aryl})_2]^-$ anions are held together by $[\text{Li}(\text{ligand})_2]^+$ cations. We have at present no evidence as to whether these $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ aggregates remain intact in solution. The literature of Li^+/π -arene interactions is extensive,³⁰ and in those structures and the Li^+ ions are almost invariably further coordinated by oxygen atoms (usually from ether-type molecules)

or nitrogen atoms (from amine ligands). In the title compound, no such additional coordination is observed. The Li atoms in $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ are surrounded only by a sheath of π -electrons of the three phenyl rings.

The $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$ cation has a remarkable structure consisting of four edge-bridging Li atoms and two triply bridging Li atoms surrounding a parallelogram made up of four bromine atoms (Figure 3). Each edge-bridging Li atom is solvated by two ether molecules, and each triply bridging Li atom is solvated by one ether molecule (Figure 2). There is an inversion center at the center of the cation as shown on Figure 3. The whole cation displays the basic feature inherited from a LiBr crystal which has a NaCl-type structure. One can view the cation skeleton as though it were a quarter of a unit cell of a LiBr crystal with two Br atoms removed (see below).



The average Li–Br distance, 2.58 (2) Å, is shorter than the average distance in lithium bromide itself, 2.748 (4) Å.³¹ But it is very close to the Li–Br distance in the recently discovered cluster $[(\text{PhLi}(\text{Et}_2\text{O})_3)_3\text{LiBr}]$ (2.54 Å).¹¹ The Br...Br distance found here, 3.884 (3) Å, is also very close to that found by EXAFS spectroscopy for the Li_4Br_4 cluster in ether solution [3.87 (2) Å].³²

What we have here, therefore, is an aggregate which can best be described as a small fragment of a LiBr salt crystal, solvated by ether molecules. Not many of such "salt clusters" are known, but the list is growing and the present cluster, $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}$, represents the largest one structurally characterized to date. The $[\text{Li}_4\text{Cl}_4(\text{Et}_2\text{O})_{10}]^{2+}$ aggregate, also a dication, was reported recently,¹⁶ as was the neutral $[\text{Li}_4\text{Cl}_4(\text{HMPa})_4]$ [HMPa = $\text{OP}(\text{NMe}_2)_3$].³³ The latter compound shows a cubane-like Li_4Cl_4 central core. In addition, EXAFS studies³² on LiBr in Et_2O support the existence of Li_4Br_4 tetramers (presumably also ether solvated) in solution. One can speculate that these "salt clusters", particularly the ether-solvated ones,^{16,33,34} represent the early stages of nucleation and growth of a lithium halide crystal as it crystallizes from ether.

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Registry No. $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}][\text{Ag}_3\text{Li}_2\text{Ph}_6]_2$, 94889-75-5; phenyllithium, 591-51-5; silver bromide, 7785-23-1.

Supplementary Material Available: Final molecular parameters for $[\text{Li}_6\text{Br}_4(\text{Et}_2\text{O})_{10}]^{2+}[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-_2$ (atomic coordinates) (2 pages). Ordering information is given on any current masthead page.

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(17) Taken as half of the interatomic distance in silver metal; see: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, p 278.

(18) Taken as half of the interatomic distance of the Li_2 molecule; see: Clark, C. H. D. *Philos. Mag.* **1934**, *18*, 459.

(19) For other examples of nonbonding Ag...Ag distances (range 2.94–3.36 Å) that have appeared in the literature, see ref 20–25. In contrast, examples of shorter (perhaps bonding) Ag–Ag distances (range 2.74–2.92 Å) are given in ref 26 and 27. For comparison, the Ag–Ag distance in silver metal is 2.889 Å.²⁸

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