**Preparation of the Silver(I) Complex $Ag_2\mathbf{8}^{2+}$.** One hundred milligrams (0.502 mmol) of $AgBF_4$ dissolved in 40 mL of toluene was added at room temperature to a stirred suspension of **8** (120 mg, 0.600 mmol) in 80 mL of $CH_2Cl_2$.

The reaction was monitored by TLC ($SiO_2$, Kieselgel 60, 10% MeOH in $CH_2Cl_2$). After stirring, the solution was clear and colorless. After standing 2 h in the dark, white crystals appeared in the solution. They were filtered on paper, washed with 25 mL of toluene, and dried in vacuum: yield 142 mg (99%).

**$Ag_2\cdot\mathbf{8}^{2+}\cdot 2BF_4^-$:** colorless crystals (mp 288 °C, dec); $^1H$ NMR (see Table IV); MS, calculated 2312.8, found 2311.9. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Ag_2B_2F_8\cdot CH_2Cl_2\cdot H_2O$: C, 61.86; H, 4.32; N, 4.47. Found: C, 61.84; H, 4.31; N, 4.37.

**Preparation of the Zinc(II) Complex $Zn_2\cdot\mathbf{8}^{4+}$.** One hundred eleven milligrams (0.300 mmol) of $Zn(ClO_4)_2\cdot 6H_2O$ in 30 mL of EtOH was added with stirring at room temperature to a suspension of **8** (100 mg, 0.050 mmol) in $CH_2Cl_2$–$CH_3CN$ (40 mL, 40 mL).

The reaction was monitored by TLC ($SiO_2$, Kieselgel 60, 10% MeOH in $CH_2Cl_2$). After stirring for 24 h, the reaction mixture was clear and almost colorless. After evaporation of the solvents, the pale yellow solid obtained was washed with 200 mL of $H_2O$ and filtered on a sintered glass: yield 98 mg (78%). The complex could be recrystallized from $CH_3CN$–toluene, affording an analytical sample.

**$Zn_2\cdot\mathbf{8}^{4+}\cdot 4ClO_4^-$:** colorless crystals (mp 174 °C, dec); $^1H$ NMR (see Table IV); MS, calculated 2439.4, found 2439.1. Anal. Calcd for $C_{128}H_{104}N_8O_{36}Zn_2Cl_4$: C, 60.33; H, 4.10; N, 4.41. Found: C, 60.32; H, 4.21; N, 4.40.

**Preparation of the Cobalt(II) Complex $Co_2\cdot\mathbf{8}^{4+}$.** Sixty milligrams (0.164 mmol) of $Co(BF_4)_2\cdot 6H_2O$ dissolved in 10 mL of EtOH was added with stirring at room temperature to a suspension of **8** (150 mg, 0.075 mmol) in 80 mL of $CH_3CN$.

The reaction was monitored by TLC ($SiO_2$, Kieselgel 60, 10% MeOH in $CH_2Cl_2$). After stirring for 2 h, a bright orange color appeared, and the solution was clear; 80 mL of EtOH was then slowly added to the solution: a dark orange solid began to precipitate. Crude $Co_2\cdot\mathbf{8}^{4+}$ was filtered after 24 h and dried in vacuum: yield 120 mg (65%).

**$Co_2\cdot\mathbf{8}^{4+}\cdot 4BF_4^-$:** brown crystals (mp 293 °C, dec); MS, calculated 2388.6, found 2388.9. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Co_2B_4F_{16}\cdot CH_2Cl_2\cdot 2H_2O$: C, 59.66; H, 4.23; N, 4.31. Found: C, 59.63; H, 4.24; N, 4.32.

**Preparation of the Nickel(II) Complex $Ni_2\cdot\mathbf{8}^{4+}$.** One hundred eighty milligrams (0.049 mmol) of $Ni(BF_4)_2\cdot 6H_2O$ in 45 mL of EtOH was added with stirring at room temperature to a suspension of **8** (150 mg, 0.075 mmol) in 90 mL of $CH_3CN$. The reaction was monitored by TLC ($SiO_2$, Kieselgel 60, 10% MeOH in $CH_2Cl_2$). After stirring for 72 h, the pale green reaction mixture still contained undissolved ligand **8**, and no further evolution was observed. The solvents were evaporated, and crude $Ni_2\cdot\mathbf{8}^{4+}$ was washed with 150 mL of $H_2O$ and filtered on a sintered glass: yield 90 mg (49%). The complex could be recrystallized from $CH_3CN$–MeOH, affording an analytical sample.

$Ni_2\cdot\mathbf{8}^{4+}\cdot 4BF_4^-$: pale yellow crystals (mp 277 °C, dec); MS, calculated 2388.1, found 2387.2. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Ni_2B_4F_{16}\cdot MeOH\cdot H_2O$: C, 61.36; H, 4.39; N, 4.44. Found: C, 61.31; H, 4.33; N, 4.47.

**Acknowledgment.** We thank the financial contribution of the CNRS. Discussions with Dr. Jean-Marc Kern are also gratefully acknowledged as well as the Strasbourg mass spectroscopy group.

---

# Isolation and First Structural Characterization of Dimethyl Sulfide Solvates of Phenyllithium, Phenylcopper, and Lower and Higher Order Lithium Phenylcuprate Reagents

**M. M. Olmstead and P. P. Power***

*Contribution from the Department of Chemistry, University of California, Davis, California 95616.* *Received April 2, 1990*

**Abstract:** The use of dimethyl sulfide as a solvent for organocopper reagents has allowed the first X-ray structure determinations of crystalline materials isolated from the addition of phenyllithium, in various ratios, to cuprous bromide in neat dimethyl sulfide. Upon removal of the insoluble lithium bromide, solutions of the 1:1 mixture yield crystals of $[Cu_4Ph_4(SMe_2)_2]$ (**1**). Its structure has a rhombus of four coppers that are edge-bridged by phenyl groups perpendicular to the $Cu_4$ plane and displays both long and short Cu···Cu diagonal distances of 4.101 (2) and 2.717 (2) Å, respectively. Two equivalents of LiPh with CuBr affords the species $[Li_2Cu_2Ph_4(SMe_2)_3]$ (**2**), an aggregate of two $[CuPh_2]^-$ moieties bridged by two $Li^+$ ions which are solvated by one and two $SMe_2$ groups. Treatment of CuBr with 3 equiv of LiPh produces the higher order cuprate $[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$ (**3**). The first X-ray structural determination of such a species shows it to be an aggregate of $CuPh_2^-$ and $CuPh_3^{2-}$ moieties that are bridged by three $Li^+$ ions and solvated by four $SMe_2$ groups. A 10% excess over 3 equiv (3.3 equiv of LiPh per CuBr) does not give the all-trigonal higher order cuprate. Instead the larger aggregate, $[Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4]$ (**4**), is obtained. The structure of the phenyllithium precursor $[Li_4Ph_4(SMe_2)_4]$ (**5**) was also determined and found to be tetrameric, with one set of alternating corners of a cube occupied by $Li(SMe_2)$ and the other set of corners occupied by triply-bridging phenyls. It is the first structure of an organolithium thioether solvate complex that was crystallized from a thioether. The results demonstrate that it is possible to isolate higher order cuprates as crystalline materials from $Me_2S$ solutions. Furthermore, the X-ray data are consistent with previously reported $^{13}C$ NMR solution studies that indicated the presence of **1**, **2**, **3**, and **5** in solution. In addition, structural relationships between LiPh, CuPh, $LiCuPh_2$, and the higher order phenyl cuprates have now been established which show that the ions $[CuPh_2]^-$ and $[CuPh_3]^{2-}$ are the dominant structural components in the cuprates when crystallized from $Me_2S$. A possible explanation for the lack of formation of certain higher order cuprates in conventional ether solvents is also provided.

The widespread use of neutral organocopper (CuR) or diorganocuprate (usually written as $LiCuR_2$ or variations thereof) reagents in organic synthesis has led to considerable interest in their structures. Neutral organocopper compounds have been known since 1923,[1] and cuprate species were first reported in 1952.[2] Subsequently, they were introduced as reagents in organic synthesis in 1966[3] and 1967.[4] Their reactions have been extensively investigated from the organic–synthetic viewpoint, and this work has been well reviewed.[5] Inquiry into the detailed

---

[1] Reich, R. *C. R. Hebd. Seances Acad. Sci.* **1923**, *177*, 322. Gilman, H.; Straley, J. *Recl. Trav. Chim. Pays-Bas* **1936**, *55*, 821.

[2] Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630.

[3] House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128.

[4] Corey, E. J.; Posner, G. *J. Am. Chem. Soc.* **1967**, *89*, 3111.

0002-7863/90/1512-8008$02.50/0

structures of the compounds has advanced less rapidly. For example, the first X-ray crystal structure of a copper(I) alkyl, the tetrameric species $[CuCH_2SiMe_3]_4$, was only reported in 1973.[6] An X-ray structure of only one other neutral copper(I) alkyl, the dimeric $[\{CuC(SiMe_3)_2(2\text{-}C_5H_4N)\}_2]$, has been published since.[7] In addition, there is, at present, no detailed structural characterization of a lithium dialkyl cuprate corresponding to the dimeric planar $Li_2Cu_2R_4$ model which is widely held to be correct and is supported by spectroscopy in solution.[8] However, structures of the lithium dialkyl cuprate salts $[Li(THF)_4][Cu\{C(SiMe_3)_3\}_2]$,[9] $[Li(12\text{-crown-}4)_2][CuMe_2]$,[10] and $[Cu(dmpe)][CuMe_2]$[11] have appeared, but these are not thought to have an exact structural resemblance to common lithium organocuprates owing to the presence of complexing reagents or very bulky copper substituents. Arylcopper and diaryl cuprate derivatives have proved more tractable to structural investigation. For arylcopper species, crystalline derivatives thought to be $[(CuPh)_4{\cdot}PhLi{\cdot}3.5Et_2O]$ were reported as early as 1966.[12] It was later shown that this compound probably corresponded to the structure $[Cu_5Ph_6][Li(THF)_4]$[13] (vide infra). The first arylcopper structures, the tetramers $[CuAr]_4$ featuring the chelating ligand $-C_6H_3(4\text{-Me})\text{-}2\text{-}CH_2NMe_2$, were reported in 1972.[14,15] Further related arylcopper derivatives involving various ligands, degrees of aggregation, or the inclusion of co-ligands such as halides or acetylides have also been reported.[5e,16] More recently, the structures of the pentameric mesitylcopper, $[CuMes]_5$,[16] the tetramer $[(CuMes)_4(THT)_2]$ (THT = tetrahydrothiophene),[17] the tetramer $[Cu_4(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$,[18] featuring asymmetric Cu–C bonds, and the remarkable monomeric species $[CuC_6H_22,4,6\text{-}Ph_3]$[19] have been published.

For lithium diarylcuprate derivatives less structural data have appeared. Solution $^1H$ NMR studies on $[Li_2Cu_2(C_6H_4\text{-}2\text{-}CH_2NMe_2)_4]$[20] and related species indicated a neutral $Li_2Cu_2$ core which was later confirmed by X-ray data.[21] Disproportionation experiments on mesitylcopper also afforded the species $[Cu(dppe)_2][CuMes_2]$[22] featuring a linear structure for the ion $[CuMes_2]^-$. The first X-ray structure of a cuprate featuring both lithium and copper in the same metal framework involved the species $[Li_2Cu_3Ph_6]^-$.[23] This structure displays a trigonal-bipyramidal metal framework and may be described as an aggregation of three $[CuPh_2]^-$ ions bridged by two axial lithium ions. With one lithium counter cation its formula corresponds exactly to solvated "$LiCuPh_2$". The recurrence of the $[CuPh_2]^-$ structural motif with different counter cations, for example, $[Li(THF)_4]^+$,[13,24] $[Li(Et_2O)_4]^+$,[25] or $[Li_4Cl_2(OEt_2)_{10}]^{2+}$,[23] and with different bridging atoms in the apical positions as in $[Cu_5Ph_6]^-$[13] or $[LiCu_4Ph_6]^-$[25] supports the view that they possess different structures from the dimeric lithium cuprate derivatives with chelating aryl ligands.[20]

Two further aspects of organocopper/cuprate chemistry are of relevance to the structural studies in this paper. First, the addition of more than 2 equiv of the lithium reagent LiR to a copper halide can result in a "higher order" organocuprate, the simplest of which may be written as "$Li_2CuR_3$". Such compounds were first proposed in 1972[26] in the case of $Li_2CuPh_3$ to account for the increased reactivity when more than 2 eqiuv of LiPh were added to the copper halide. However, the structures of $Li_2CuR_3$ compounds are the subject of some controversy with considerable divergence of opinion on whether $Li_2CuR_3$ is a separate entity or a mixture of $LiCuR_2$ and LiR.[27] Second, although most organocopper compounds are commonly prepared in ether or THF, the solubility of copper halides in thioethers has led to the investigation and use of such solvents as an alternative to ethers.[28] Most recently, it has been shown that dimethyl sulfide ($Me_2S$) possesses considerable advantages over $Et_2O$ or THF from the standpoint of reactivity and stability.[29] In addition, dimethyl sulfide solvent has permitted the first spectroscopic ($^{13}C$ NMR) identification of the higher order cuprate ion $[CuPh_3]^{2-}$ in solution.[30] It was these interesting results that prompted the investigations in this paper.

The main objective of this work was to investigate the crystalline products arising from the addition of different numbers of equivalents of LiPh to CuBr in dimethyl sulfide solutions. Furthermore, it was intended that this work would answer several important questions regarding cuprates that were hitherto unanswered. These are as follows: (a) Is it possible to isolate crystals involving the higher order cuprate ion $[CuPh_3]^{2-}$? (b) Are the structures of cuprates, crystallized from $Et_2O$ or THF mixtures, the same as those obtained from $Me_2S$? (c) Are there major differences between the structures of organolithium reagents, such as LiPh, when crystallized from $Et_2O$ versus $Me_2S$ solutions? (d) What is the structural relationship between the species LiAr, CuAr, $LiCuAr_2$, and $Li_2CuAr_3$ with simple rather than chelating aryl groups? (e) Is it possible to obtain the structures of more complex organocuprates such as $Li_3Cu_2Ph_5$ or related species? The results of these investigations are now described.

## Experimental Section

**General Procedures.** All reactions were performed by using modified Schlenk techniques under an inert atmosphere of $N_2$. Solvents were freshly distilled from drying agents, hexane from Na/K and dimethyl sulfide from LAH, and degassed prior to their use. Halide free phenyllithium was prepared according to a literature procedure.[31] High purity copper(I) bromide was purchased commercially and used as received.

**$Cu_4Ph_4(SMe_2)_2$, 1.** Phenyllithium (0.84 g, 10 mmol) in $Me_2S$ (10 mL) was added dropwise to a solution of CuBr (1.43, 10 mmol) in $Me_2S$ (15 mL) cooled in an ice bath. The addition resulted in a white precipitate

---

(5) (a) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980. (b) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. (c) Normant, J. F. *Syntheses* **1972**, 63. (d) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215. (e) van Koten, G.; Noltes, J. G. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1984; Vol. 1, Chapter 14.

(6) Jarvis, J. A.; Kilbourn, B. T.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 475.

(7) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1419.

(8) Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. Stewart, K. R.; Lever, J. R.; Whangbo, M.-H. *J. Org. Chem.* **1982**, *47*, 1472. The first structure of a lithium dialkylcuprate aggregate has been determined recently in this laboratory: Olmstead, M. M.; Power, P. P. *Organometallics* **1990**, *9*, 1720.

(9) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23.

(10) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337.

(11) Dempsey, D. F.; Girolami, G. S. *Organometallics* **1989**, *7*, 1208.

(12) Costa, G.; Camus, A.; Gatti, L.; Marsich, N. *J. Organomet. Chem.* **1966**, *5*, 568.

(13) Edwards, P. G.; Gellert, R. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072.

(14) Guss, J. M.; Mason, R.; Søtofte, I.; van Koten, G.; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* **1972**, 446.

(15) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 129.

(16) Guss, J. M.; Mason, R.; Thomas, J. M.; van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1972**, *40*, C79. van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551. ten Hoedt, R. W. M.; Noltes, J. G.; van Koten, G.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1804.

(17) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156. Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8* 1067.

(18) Nobel, D.; van Koten, G. A.; Spek, L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 208.

(19) Lingnau, R.; Strahle, J. *Angew. Chem.* **1988**, *100*, 409.

(20) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1978**, *101*, 6593.

(21) van Koten, G.; Jastrzebski, T. B. H.; Muller, F.; Stam, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 697.

(22) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240.

(23) Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149.

(24) Olmstead, M. M.; Power, P. P. Unpublished results.

(25) Khan, S. I.; Edwards, P. G.; Xuan, H. S.; Bau, R. *J. Am. Chem. Soc.* **1985**, *107*, 1682.

(26) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

(27) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 784; **1977**, *99*, 5312. Lipshutz, B. H.; Kozlowski, J. A.; Breneman, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197. Lipshutz, B. H.; Kozlowski, J.; Floyd, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 7672.

(28) Corey, E. J.; Corney, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 7318. Clark, R. D.; Heathcock, C. H. *Tetrahedron Lett.* **1974**, 1713. House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.

(29) Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989**, *45*, 425.

(30) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668.

(31) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.

(LiBr) and a yellow solution. Stirring was continued for 1 h, and all the solvents were removed under reduced pressure. $Me_2S$ (15 mL) and hexane (10 mL) were added, and the solution was filtered through Celite. The volume was reduced to ca. 15 mL, and the solution was cooled in a -20 °C freezer overnight to give the product **1** as yellow crystals: yield 1.1 g, 64%; mp 96–98 °C dec.

**$Li_2Cu_2Ph_4(SMe_2)_3$,2.** Phenyllithium (1.68 g, 20 mmol) in $Me_2S$ (20 mL) was added dropwise to a solution of CuBr (1.43 g, 10 mmol) in $Me_2S$ (15 mL) cooled in an ice bath. The addition gave a white precipitate (LiBr) and a yellow solution. Hexane (10 mL) was added, and the solution was stirred for a further 1 h and filtered through Celite. The volume of the filtrate was then reduced to ca. 20 mL and cooled overnight in a -20 °C freezer to give the product **2** as yellow crystals: yield 1.9 g, 60%.

**$Li_3(CuPh_2)(CuPh_3)(SMe_2)_4$, 3.** Phenyllithium (1.36 g, 16.2 mmol) in $SMe_2$ (20 mL) was added dropwise to a solution of CuBr (0.77 g, 5.4 mmol) in $SMe_2$ (15 mL) with cooling in an ice bath. The solution was stirred for 1 h and then slowly filtered through Celite. The yellow-orange filtrate was reduced in volume to 7–8 mL and filtered again. Cooling in a -20 °C freezer for 40–50 days gave the product **3** as yellow-orange crystals: yield 1.o g, 62%. This compound has also been reported in a preliminary communication.[32]

**$Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4$, 4.** The compound **4** was synthesized by a procedure very similar to that for **1** with 3.3 equiv of PhLi for CuBr. Attempts to accelerate crystal growth of **1** or a related species by the addition of hexane (25%) to the filtrate in the procedure for **1** resulted in the deposition of yellow crystals of **4** in about 40% yield.

**$Li_4Ph_4(SMe_2)_4$, 5.** Phenyllithium (1.68 g, 20 mmol) was dissolved in $Me_2S$ (25 mL) with cooling in an ice bath. The volume of the solution was lowered to ca. 15 mL under reduced pressure. Hexane (10 mL) was added, and the solution was filtered. The volume of the solution was reduced to incipient crystallization (ca. 20 mL). Cooling in a -20 °C freezer overnight afforded the product **5** as colorless crystals: yield 2.1 g, 72%.

**Data Collection and Crystal Data Processing.** Crystals of these compounds were protected from air oxidation and loss of dimethyl sulfide by coating them with a hydrocarbon oil and quickly mounting them in the cold stream of the diffractometer. This technique has been previously described.[33]

Data collection for compounds **2** and **5** was carried out on a Syntex $P2_1$ diffractometer, while for **1** and **4** a Siemens R3 diffractometer was used. Crystal data for **3** has already been reported.[32] In each case, data was collected at 130 K with use of ω-scans, Mo Kα radiation (λ = 0.71069 Å), and a graphite monochromator. No loss in intensity of check reflections was observed during the course of data collection. The data were corrected for absorption with use of program XABS.[34] Atomic scattering factors were taken from the *International Tables*.[35] Crystallographic programs used were those of SHELXTL, Version 5, installed on a Data General Eclipse computer (**2** and **5**) and Siemens SHELTXL PLUS installed on a MicroVAX 3200 (**1** and **4**).

Crystal data are as follows: **1**, $Cu_4Ph_4(SMe_2)_2$, $C_{28}H_{32}Cu_4S_2$, $a$ = 7.355 (2) Å, $b$ = 9.773(2) Å, $c$ = 10.396(3) Å, $\alpha$ = 68.81(2)°, $\beta$ = 82.29(2)°, $\gamma$ = 71.89(2)°, $Z$ = 1, space group $P\bar{1}$ 2447 unique observed data with $I > 2\sigma(I)$, $R$ = 0.065; **2**, $Li_2Cu_2Ph_4(SMe_2)_3$, $C_{30}H_{38}Cu_2Li_2S_3$, $a$ = 13.115 (4) Å, $b$ = 16.070 (4) Å, $c$ = 15.242 (4) Å, $\beta$ = 106.56 (2)°, $Z$ = 4, space group $P2_1/n$, 4551 unique observed data with $I > 2\sigma(I)$, $R$ = 0.031; **4**, $C_{62}H_{69}Cu_4Li_5S_4$, $a$ = 34.116 (11) Å, $b$ = 12.786 (3) Å, $c$ = 27.850 (6) Å, $\beta$ = 94.04 (2)°, $Z$ = 8, space group $C2/c$, 5169 unique observed data with $I > 2\sigma(I)$, $R$ = 0.068; **5**, $Li_4Ph_4(SMe_2)_4$, $C_{32}H_{44}Li_4S_4$, $a$ = 11.538 (2) Å, $b$ = 11.703 (2) Å, $c$ = 15.641 (3) Å, $\alpha$ = 73.12 (1)°, $\beta$ = 69.37 (1)°, $\gamma$ = 61.13°, $Z$ = 2, space group $P\bar{1}$, 4950 unique observed data with $I > 2\sigma(I)$, $R$ = 0.046.

## Results

The title compounds **1–5** were synthesized under anaerobic and anhydrous conditions by straightforward procedures. Halide free LiPh[31] was used for all the syntheses to avoid possible complications or contamination with halide anions. Crystallization of all compounds except **3** could be accomplished by overnight cooling in a -20 °C freezer. The compound **3** crystallized slowly over a period of several weeks.

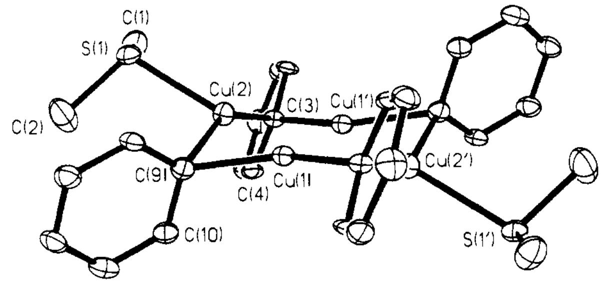


**Figure 1.** A computer-generated drawing of $[Cu_4Ph_4(SMe_2)_2]$, **1**, showing the atom-numbering scheme. Anisotropic thermal ellipsoids are drawn at the 50% probability level.

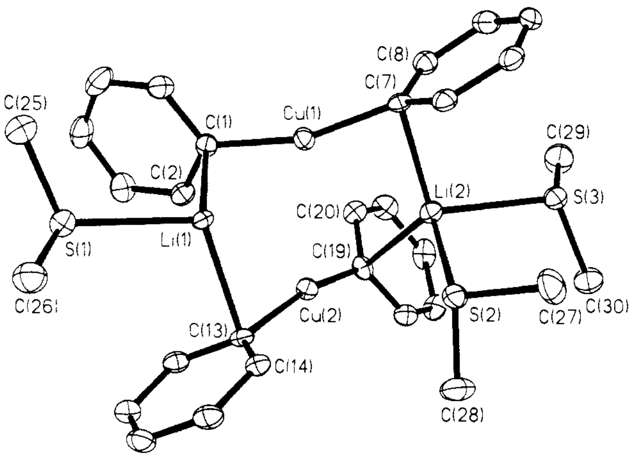


**Figure 2.** A computer-generated drawing of $[Li_2Cu_2Ph_4(SMe_2)_3]$, **2**, showing the atom-numbering scheme. Anisotropic thermal ellipsoids are drawn at the 50% probability level.

**Structural Descriptions of 1–5. $Cu_4Ph_4(SMe_2)_2$, 1.** The 1:1 product crystallizes in high yield from either dilute or concentrated dimethyl sulfide solutions to form the centrosymmetric $Cu_4$ species pictured in Figure 1. A summary of the important bond distances and angles is presented in Table I. The Cu–Cu sides are nearly equal (2.444 (2) and 2.475 (1) Å), but the Cu–Cu–Cu angles (113.0 (1)° and 67.0 (1)°) differ greatly. Thus, the four coplanar coppers describe a rhombus with one short 2.717 (2) Å and one long 4.101 (1) Å, diagonal Cu···Cu vector. Each Cu···Cu edge is bridged by a phenyl ring perpendicular to the $Cu_4$ plane. Nonetheless, the ipso carbons are not coplanar with the $Cu_4$ array but are disposed in mutually adjacent pairs above and below the plane. The $SMe_2$ groups are anti with respect to the phenyl ring substituents on the copper to which it is bonded. Although the molecule has a center of symmetry, there is also a noncrystallographic 2-fold axis passing through the Cu(1)···Cu(1′) line. The Cu–C distances display slight asymmetry with the longer 2.062 Å bonds associated with Cu(2) and the shorter 2.004 Å bonds associated with Cu(1). The Cu–S distance is 2.383 (2) Å.

**$Li_2Cu_2Ph_4(SMe_2)_3$, 2.** The crystallographic results for the $LiCuR_2$ cuprate show the association of two $CuPh_2^-$ units bridged by two $Li^+$ ions in the solid state (Figure 2). Selected distances and angles are given in Table I. The Cu···Cu distance is 2.869 (1) Å. One lithium is solvated by one $SMe_2$, and the other lithium is solvated by two $SMe_2$ groups. The integrity of the linear $CuPh_2^-$ species in **2** can be appreciated from the C–Cu–C angles of 162.2 (1)° and 163.5 (1)° for Cu(1) and Cu(2), respectively. Further, there is only a small dihedral angle averaging 10.5° between the Cu–C bonds and their respective phenyl rings. In contrast, the angles between the Li–C bond and the phenyl planes average 108.5°. The average Cu–C distance is 1.937 (3) Å, and the average Li–C(ipso) bond is 2.284 (5) Å long. Distances of the Li to the ortho carbons span the range of 2.830 (5) to 3.066 (5). The Li centers are essentially equivalent with respect to the cluster,

---

[32] Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4135.

[33] Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

[34] Program XABS. The method provides an empirical correction based on $F_o$ and $F_c$ differences: Hope, H.; Moezzi, B. Chemistry Department, University of California, Davis.

[35] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

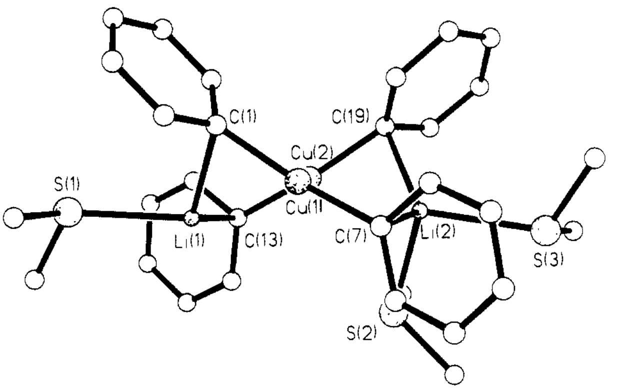


**Figure 3.** Compound **2** viewed down the Cu–Cu line showing the staggering of the $CuPh_2^-$ units and the bridging geometry. Atoms are drawn with a size proportional to their covalent radii.

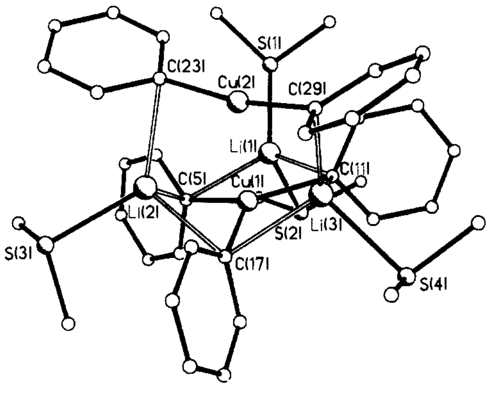


**Figure 4.** Compound **3**, $[Li_3(CuPh_3)(CuPh_2)(SMe_2)_4]$.

as Figure 3 demonstrates when the structure is viewed down the Cu···Cu bond. If the $SMe_2$ groups are ignored, the structure has 2-fold symmetry about a vertical axis passing through the Cu···Cu line. This view displays the staggering of the linear C–Cu–C units and dihedral angles of 62.8° for C(1)–Cu(1)–Cu(2)–C(13) and 61.4° for C(7)–Cu(1)–Cu(2)–C(19). The fold angle of the $Cu_2Li_2$ butterfly is 145.9°.

**$[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$, 3.** The asymmetric unit consists of two chemically identical but crystallographically independent molecules corresponding to the above formula. The structure, illustrated by one of the molecules in Figure 4, may be described as a combination of the entities $[CuPh_2]^-$ and $[CuPh_3]^{2-}$ linked by three bridging $Li^+$ ions. Important bond distances and angles are provided in Table I. There are also good reasons (vide infra) for considering the structure as an association of the ions $[Li_3CuPh_3(SMe_2)_4]^+$ and $[CuPh_2]^-$. Whichever viewpoint is adopted the $[CuPh_3]^{2-}$ moiety has an average Cu–C distance of ~2.02 Å and the sum of the angles at Cu(1) is 357.1°, and the Cu atom is 0.202 Å above the $C(ipso)_3$ plane. Also, the three phenyl rings are approximately perpendicular to the $CuC(ipso)_3$ plane. The angle at Cu(2) is 164.6 (2)° and the average Cu–C distance is 1.93 Å. Here, there are different dihedral angles between the Cu–C bonds and the phenyl planes (8° and 21.5°) in the case of the C(23) and C(29) rings. Two $Li^+$ ions bridge two ipso carbons from $[CuPh_3]^{2-}$ and an ipso carbon from the $[CuPh_2]^-$ moieties. These $Li^+$ centers are solvated by a single $SMe_2$ molecule. The remaining $Li^+$ ion bridges two ipso carbons from the $[CuPh_3]^{2-}$ group exclusively with no interaction with the $[CuPh_2]^-$ group. This $Li^+$ center is solvated by two $SMe_2$ molecules. The Li–C and Li–S bond distances are quite variable (see Table I) and may be rationalized on the basis of coordination number or the relative strength of the interaction to the various coordinated ligands.

**$[Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4]$, 4.** This unusual aggregate is comprised of three linear $[CuPh_2]^-$ ions triply bridged by two lithiums and one trigonal, higher order $CuPh_3^{2-}$ unit associated with three lithiums and solvated by four $SMe_2$ molecules. Figure

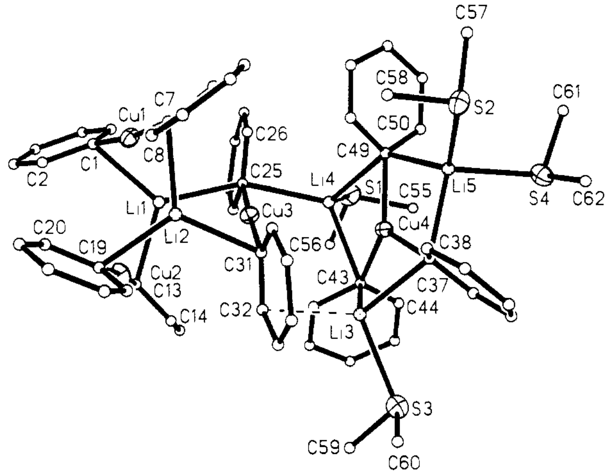


**Figure 5.** A computer-generated drawing of $[Li_5Cu_4Ph_9(SMe_2)_4]$, **4**, showing the atom-numbering scheme. Anisotropic thermal ellipsoids are drawn at the 50% probability level. Carbon and lithium atoms are drawn with an arbitrary size to reduce the clutter of the drawing.

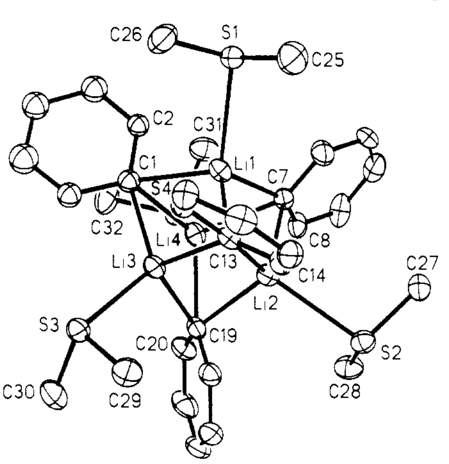


**Figure 6.** A computer-generated drawing of $[LiPh(SMe_2)]_4$, **5**, showing the atom-numbering scheme. Anisotropic thermal ellipsoids are drawn at the 50% probability level.

5 depicts the constituents of this isolated aggregate, while selected bond lengths and angles are listed in Table I. The trigonal-bipyramidal $[Li_2Cu_3Ph_6]^-$ ion is quite flattened, with long Cu···Cu distances of 3.482 (2), 3.669 (2), and 3.630 (2) Å and a Li···Li distance of 3.43 (2) Å. All the Cu–C distances are fairly uniform and average 1.93 (1) Å.

The $[Li_2Cu_3Ph_6]^-$ moiety is linked to the remaining $[Li_3CuPh_3(SMe_2)_4]^+$ section primarily via the Li(4)–C(25) interaction of 2.39 (2) Å length and an unusual Li–C(ortho) interaction of 2.56 (2) Å between Li(3) and C(32). All other Li–C distances are much longer, the next shortest being Li(3)–C(31) of 3.02 (2) Å. The distance Cu(3)···Cu(4) is 3.492 (2) Å and is apparently not attractive, as Cu(4) is displaced in a direction away from Cu(3) in the $CuLi_3$ plane. The C–Cu–C angles at Cu(4) of 112.7 (4), 127.2 (4), and 118.2 (4)° and Li–Cu–Li angles of 114.1 (6), 123.4 (6), and 120.7 (6)° aproximate trigonal-planar geometry at Cu(4).

Each of the three Li atoms approaches the bridging phenyls from the side, and for this reason the planes of the phenyl rings are roughly perpendicular to the $Li_3Cu$ plane. In addition, each Li atom has two other interactions: Li(4) to C(25) and S(1); Li(3) to C(32) and S(3); and Li(5) to S(2) and S(4). Thus, these latter three lithium atoms display tetrahedral geometry while Li(1) and Li(2) are trigonal.

**$Li_4Ph_4(SMe_2)_4$, 5.** The lithium aryl thioether solvate is tetrameric as illustrated in Figure 6. Bond lengths and angles are summarized in Table I. The structure may be described as a tetrahedron of four lithium atoms with each face bridged by the ipso carbon of a phenyl ring. Each lithium atom is further solvated

**Table I.** Important Interatomic Distances (Å) and Angles (deg) in Compounds **1–5**

| | | | | | |
|---|---|---|---|---|---|
| Compound **1** | | | | | |
| Cu(1)–C(9) | 1.997 (8) | Cu(2)···Cu(2′) | 4.101 (2) | | |
| Cu(1)–C(3′) | 2.010 (6) | Cu(1)···Cu(1′) | 2.717 (2) | | |
| Cu(2)–C(3) | 2.054 (6) | Cu(1)···Cu(2′) | 2.475 (1) | | |
| Cu(2)–C(9) | 2.070 (6) | Cu(1)···Cu(2′) | 2.444 (2) | | |
| Cu(2)–S(1) | 2.383 (2) | | | | |
| C(3′)–Cu(1)–C(9) | 144.3 (3) | Cu(1)–Cu(3)–Cu(2) | 73.9 (2) | | |
| C(3)–Cu(2)–C(9) | 146.0 (2) | Cu(2)–Cu(1)–Cu(2′) | 113.0 (1) | | |
| Cu(1)–C(9)–Cu(2) | 74.9 (3) | Cu(1′)–Cu(2)–Cu(1) | 67.0 (1) | | |
| Compound **2** | | | | | |
| Cu(1)–C(1) | 1.937 (3) | S(3)–Li(2) | 2.526 (5) | | |
| Cu(1)–C(7) | 1.934 (3) | C(1)–Li(1) | 2.297 (5) | | |
| Cu(2)–C(13) | 1.938 (3) | C(7)–Li(2) | 2.267 (5) | | |
| Cu(2)–C(19) | 1.940 (2) | C(13)–Li(1) | 2.302 (5) | | |
| S(1)–Li(1) | 2.524 (5) | C(19)–Li(2) | 2.268 (6) | | |
| S(2)–Li(2) | 2.552 (5) | | | | |
| C(1)–Cu(1)–C(7) | 162.2 (1) | Cu(2)–C(13)–Li(1) | 84.8 (1) | | |
| C(13)–Cu(2)–C(19) | 163.5 (1) | Cu(2)–C(19)–Li(2) | 82.8 (1) | | |
| C(1)–Li(1)–C(13) | 115.6 (2) | S(1)–Li(1)–C(1) | 103.6 (2) | | |
| C(7)–Li(2)–C(19) | 120.0 (2) | S(1)–Li(1)–C(13) | 108.8 (2) | | |
| Cu(1)–C(1)–Li(1) | 79.6 (2) | S(2)–Li(2)–S(3) | 96.7 (2) | | |
| Cu(1)–C(7)–Li(2) | 84.1 (2) | | | | |
| Compound **3** | | | | | |
| Cu(1)–C(5) | 2.039 (4) | C(5)–Li(2) | 2.380 (9) | | |
| Cu(1)–C(11) | 2.000 (4) | C(11)–Li(1) | 2.278 (9) | | |
| Cu(1)–C(17) | 2.032 (4) | C(11)–Li(3) | 2.353 (8) | | |
| Cu(2)–C(23) | 1.916 (5) | C(17)–Li(2) | 2.402 (10) | | |
| Cu(2)–C(29) | 1.942 (4) | C(17)–Li(3) | 2.394 (8) | | |
| S(1)–Li(1) | 2.497 (8) | C(23)–Li(2) | 2.409 (8) | | |
| S(2)–Li(1) | 2.479 (8) | C(28)–Li(2) | 2.450 (10) | | |
| S(3)–Li(2) | 2.459 (7) | C(29)–Li(3) | 2.274 (9) | | |
| S(4)–Li(3) | 2.445 (9) | Cu(1)···Cu(2) | 3.019 | | |
| C(5)–Li(1) | 2.308 (8) | | | | |
| C(5)–Cu(1)–C(11) | 120.5 (2) | C(11)–Cu(1)–C(17) | 122.3 (2) | | |
| C(5)–Cu(1)–C(17) | 114.3 (2) | C(23)–Cu(2)–C(29) | 164.6 (2) | | |
| Compound **4** | | | | | |
| Cu(1)–C(1) | 1.94 (1) | Li(1)–C(1) | 2.33 (2) | Li(3)–C(43) | 2.31 (2) |
| Cu(1)–C(7) | 1.92 (1) | Li(1)–C(13) | 2.29 (2) | Li(4)–S(1) | 2.53 (2) |
| Cu(2)–C(13) | 1.93 (1) | Li(1)–C(25) | 2.32 (2) | Li(4)–C(25) | 2.39 (2) |
| Cu(2)–C(19) | 1.92 (1) | Li(2)–C(7) | 2.27 (2) | Li(4)–C(43) | 2.42 (2) |
| Cu(3)–C(25) | 1.94 (1) | Li(2)–C(19) | 2.26 (2) | Li(4)–C(49) | 2.46 (2) |
| Cu(3)–C(31) | 1.91 (1) | Li(2)–C(31) | 2.33 (2) | Li(5)–S(2) | 2.55 (2) |
| Cu(4)–C(37) | 2.03 (1) | Li(3)–S(3) | 2.50 (2) | Li(5)–S(4) | 2.51 (2) |
| Cu(4)–C(43) | 2.00 (1) | Li(3)···C(32) | 2.56 (2) | Li(5)–C(37) | 2.32 (2) |
| Cu(4)–C(49) | 2.02 (1) | Li(3)–C(37) | 2.31 (2) | Li(5)–C(49) | 2.23 (2) |
| C(1)–Cu(1)–C(7) | 173.1 (4) | C(1)–Li(1)–C(25) | 126.2 (8) | | |
| C(13)–Cu(2)–C(19) | 174.6 (4) | C(13)–Li(1)–C(25) | 117.3 (8) | | |
| C(25)–Cu(3)–C(31) | 175 (4) | C(7)–Li(2)–C(19) | 119.8 (9) | | |
| C(37)–Cu(4)–C(43) | 112.7 (4) | C(7)–Li(2)–C(31) | 118.8 (8) | | |
| C(37)–Cu(4)–C(49) | 118.2 (4) | C(19)–Li(2)–C(31) | 121.4 (8) | | |
| C(43)–Cu(4)–C(49) | 127.2 (4) | C(37)–Li(5)–C(49) | 99.6 (8) | | |
| C(1)–Li(1)–C(13) | 116.3 (8) | | | | |
| Compound **5** | | | | | |
| S(1)–Li(1) | 2.635 (4) | Li(1)–C(13) | 2.236 (6) | Li(3)–C(13) | 2.252 (6) |
| S(2)–Li(2) | 2.616 (4) | Li(2)–C(7) | 2.241 (6) | Li(3)–C(19) | 2.244 (5) |
| S(3)–Li(3) | 2.576 (4) | Li(2)–C(13) | 2.246 (6) | Li(4)–C(1) | 2.234 (5) |
| S(4)–Li(4) | 2.588 (6) | Li(2)–C(19) | 2.269 (5) | Li(4)–C(7) | 2.268 (5) |
| Li(1)–C(1) | 2.272 (5) | Li(3)–C(1) | 2.308 (6) | Li(4)–C(19) | 2.284 (5) |
| Li(1)–C(7) | 2.271 (5) | | | | |
| S(1)–Li(1)–C(1) | 109.5 (2) | C(1)–Li(4)–C(19) | 109.9 (2) | | |
| S(1)–Li(1)–C(7) | 117.6 (2) | C(7)–Li(4)–C(19) | 105.4 (2) | | |
| Li(3)–C(19)–Li(4) | 67.8 (2) | Li(1)–C(1)–Li(3) | 69.0 (2) | | |
| C(1)–Li(1)–C(7) | 107.5 (3) | Li(1)–C(1)–Li(4) | 68.4 (2) | | |
| S(1)–Li(1)–C(13) | 107.3 (2) | Li(3)–C(1)–Li(4) | 67.5 (2) | | |
| C(1)–Li(1)–C(13) | 107.3 (2) | Li(1)–C(7)–Li(2) | 69.3 (2) | | |
| C(7)–Li(1)–C(13) | 107.2 (2) | Li(1)–C(7)–Li(4) | 67.9 (2) | | |
| C(7)–Li(2)–C(13) | 107.9 (2) | Li(2)–C(7)–Li(4) | 70.1 (2) | | |
| C(7)–Li(2)–C(19) | 106.8 (3) | Li(1)–C(13)–Li(2) | 69.8 (2) | | |
| C(13)–Li(2)–C(19) | 106.3 (2) | Li(1)–C(13)–Li(3) | 70.6 (2) | | |
| C(1)–Li(3)–C(13) | 105.5 (2) | Li(2)–C(13)–Li(3) | 70.2 (2) | | |
| C(1)–Li(3)–C(19) | 108.7 (3) | Li(1)–C(13)–C(14) | 134.1 (2) | | |
| C(13)–Li(3)–C(19) | 106.9 (2) | Li(2)–C(19)–Li(3) | 69.9 (2) | | |
| C(1)–Li(4)–C(7) | 109.0 (2) | Li(2)–C(19)–Li(4) | 69.3 (2) | | |

by one $SMe_2$ molecule which results in a distorted tetrahedral coordination for lithium.

## Discussion

The series of compounds **1–5** represents the first opportunity to study the detailed structures of the widest range of closely related solvates in which Li, Cu, or Ph are present in different proportions, and the resultant aggregates correspond to the formulas of reagents which are synthetically relevant. The use of the dimethyl sulfide solvent has played a key role in the isolation of this series of compounds. This solvent has been demonstrated to enhance both the stability and reactivity of organocopper reagents in comparison to $Et_2O$ or THF.[29] In addition, it has been shown by NMR studies that the previously unobserved higher order cuprate species $[CuPh_3]^{2-}$ is present in $SMe_2$ solutions of the reaction between CuBr and 3 equiv of LiPh.[30] In fact, the $^{13}C$ NMR spectrum of a 3:1 solution of LiPh/CuBr in $Me_2S$ shows two ipso carbon peaks for which the ratio of intensities is 3:2. These signals were assigned to the species $[CuPh_3]^{2-}$ and $[CuPh_2]^-$ which leads to the supposition that they are present in a 1:1 ratio. This assignment corresponds very closely to the formula of **3**. No analogous species could be obtained in either $Et_2O$ or THF solvent.[40] The first X-ray crystal structure of the higher order cuprate derived from this solution, the compound **3**, $[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$, was reported recently in a preliminary note.[32]

The excellent solvating properties of dimethyl sulfide underline its ability to dissolve both LiPh and CuPh.[29] In sharp contrast CuPh is practically insoluble in $Et_2O$. This solubility in $SMe_2$ allows both the complexes **1** and **5** to be isolated as single crystals and characterized by X-ray crystallography. Similarly, the conventional or lower order cuprate complex **2** corresponding to the formula $LiCuR_2$, can be obtained readily from the reaction of 2 equiv of LiPh with CuBr in $SMe_2$. Attempts to obtain a higher order cuprate corresponding exactly to the formula $Li_2CuPh_3(SMe_2)_n$ have failed so far. One reaction mixture involving more than a 3:1 ratio of LiPh/CuBr afforded the higher order cuprate **4**. Further experiments directed at the isolation of other higher order cuprates are in progress.

**$Li_4Ph_4(SMe_2)_4$, 5, $Cu_4Ph_4(SMe_2)_2$, 1, and $Li_2Cu_2Ph_4(SMe_2)_3$, 2.** The tetrameric $Li_4Ph_4(SMe_2)_4$ complex **5** bears a close structural resemblance to the corresponding species $Li_4Ph_4(Et_2O)_4$ that was crystallized from $Et_2O$.[36] The Li–C distances in the latter average 2.33 Å long. In **5**, however, the corresponding average distance is 2.26 Å. The $Li–OEt_2$ and $Li–SMe_2$ lithium chalcogenide bond distance are 2.05 and 2.6 Å, respectively. The former distance is within the expected range; however, the Li–S distances are 0.14–0.19 Å longer than predicted.[37] These data therefore point to a "tighter" $Li_4C_4$ aggregate in **5** owing to a weaker solvation of the $Li^+$ ion by the thioether ligand. A feature of the $Me_2S$ solvate of **5**, and indeed all the complexes **1–4**, is the pyramidal geometry at the donor atom. Although this result is not unexpected in the case of sulfur, it provides a sharp contrast to etherate complexes which are, almost without exception, planar at the oxygen atom. A noteworthy feature of **5** is that it appears to be the first structure of an organolithium compound that is solvated exclusively by thioethers. Phenyllithium appears to be quite stable in $SMe_2$ although quantitative studies have not yet been undertaken on its reactivity in this solvent. It may be that, in the future, $Me_2S$ may find considerable use as a solvent for organolithium reagents where the presence of oxygen donor solvents is undesirable.

The reaction of 1 equiv of LiPh with CuBr in $Me_2S$ results in an orange/yellow solution and a white precipitate (LiBr). Removal of the LiBr affords a solution which gives crystals of **1** in high yield upon cooling. Its structure is quite different from that of **5** although stoichiometrically the compounds are very similar. Presumably, the reasons for this difference involve a preference by copper, which is strongly $\sigma$-bonded to two aryl ligands, for digonal coordination and linear or near-linear geometry. These restrictions are incompatible with a tetrahedral structure similar to that of **5**. The four copper atoms are planar in contrast to the $Cu_4$ butterfly structure seen in a previously reported $(CuAr)_4$ compound with chelating aryl groups.[14] Perhaps in these cases the presence of ortho-$CH_2NMe_2$ donors distort the geometry to give a folding of the $Cu_4$ array. The structure also differs from

---

[36] Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320.

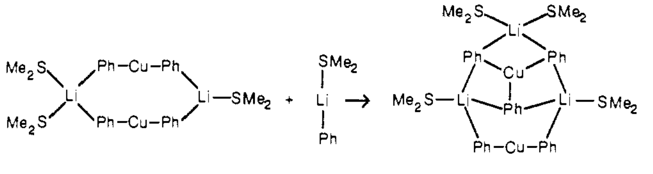
[37] Shannon, R. D. In *Structure and Bonding in Crystals*; O'Keeffe, M. K., Navrotsky, A., Eds.; Academic: New York, 1981; Vol. II, p 53. These data predict (on the basis of crystal radii derived from metal sulfides) a Li–S distance of 2.44 Å for four-coordinate $Li^+$.

that of $[(CuMes)_4(THT)_2]$[17] in two respects. First, the planar $Cu_4$ array is almost square in the mesityl compound, while in **1** there are gross distortions from this geometry to afford a rhomboidal arrangement of coppers. Second, the mesityl rings adopt an alternating pattern above and below the $Cu_4$ plane affording a distorted tetrahedral $C(ipso)_4$ array. In **1**, however, the molecule adopts a configuration where adjacent phenyl rings appear above and below the metal plane. It may be that the higher steric requirements of the mesityl group disallow the type of arrangement seen in **1**. An alternative way of viewing the structure of **1** comes from the structure of **2** which differs from **1** with the replacement of two coppers by two lithium atoms. It appears that the "long" diagonal coppers (Cu(2) and Cu(2′)) in **1** are the ones replaced by the lithium atoms in **2**. This arrangement results in a diagonal Cu⋯Cu distance of 2.869 (1) Å in **2**. This distance is only slightly longer than the corresponding "short", 2.717 (2) Å, diagonal in **1**. It is thus possible to argue that Cu(2) and Cu(2′) fulfill, to some extent, a similar role in **1** as the lithium ions do in **2** although the interaction between these coppers and the phenyl groups is much stronger than the corresponding interaction between the phenyl groups and the lithium atoms in **2**. This view receives some support from the variation in Cu–C distances in **1**. The Cu–S distance in **1**, 2.383 (2) Å, is significantly longer than that which is expected on the basis of the low copper coordination number. For example, four-coordinate $Cu^+$ ligated by thioethers has a Cu–S distance of 2.263 (6) Å.[38] The long Cu–S distance in **1** is, of course, in agreement with relatively strong competitive Cu–C bonding which may weaken any further interactions with a thioether.

Replacement of the two remaining coppers of **2** with lithium atoms results in **5**. The differences between the three structures are mainly a consequence of the different coordination preferences and bonding characteristics of Li and Cu. The formula of **2** corresponds to that of the conventional cuprate $LiCuR_2$. In the case of the phenyl ligand such compounds have already been crystallized from $Et_2O$ or THF solvent mixtures.[23,24] The resultant structure of formula $[Li_4Cl_2(OEt_2)_{10}]^+[Li_2Cu_3Ph_6]_2^-$ that was crystallized from these solvents contrasts sharply with the structure observed for **2**. It involves three $[CuPh_2]^-$ moieties associated through two $Li^+$ ions such that the metal array forms a trigonal bipyramid with two axial $Li^+$ ions and three equatorial coppers. However, the Cu–C and the Li–C bonds in this compound, 1.93 and 2.24 Å, are close to the average values, 1.938 and 2.285 Å, observed in **2**. In effect, the structures consist of similar components that are differently arranged. It appears likely that a major cause for this difference is the solvent. Ether or THF is capable of solvating the $Li^+$ ions to give $[Li_4Cl_2(OEt_2)_{10}]^+$, $[Li(Et_2O)_4]^+$, or $[Li(THF)_4]^+$[39] ions, whereas the more weakly solvating (at least for $Li^+$) $Me_2S$ is less likely to achieve the same degree of $Li^+$ solvation in the present system. Apparently, the ethers are capable of solvating one lithium ion but are not powerful enough in this respect to remove the remaining $Li^+$ ions from the $[Li_2Cu_3Ph_6]^-$ moiety when it forms. This may be due to the lower likelihood of attack on a negatively charged cluster such as $[Li_2Cu_3Ph_6]^-$ by a weakly nucleophilic $Et_2O$ group. More powerful solvating agents such as 12-crown-4 can, however, remove all the $Li^+$ ions to afford the free $[CuPh_2]^-$ species.[10] A feature of all the cuprate salts in this paper is the large difference in Li–C and Cu–C bond strengths. In all cases, where phenyl bridges Li and Cu, the angle between the Cu–C bond and the C(ipso)–C(para) vector is small (usually 10° or less), whereas the angle between the Li–C bond and the ring plane is high. For this reason the Cu–C bonds are for the most part of $\sigma$ character, whereas the $Li^+$ ion can be considered to be bonded to an orbital of $\pi$-symmetry on the phenyl ring.[21]

The question of why two $SMe_2$ ligands are present on Li(2) and only one is on Li(1) is an interesting one. It can be assumed that each Li interacts with as many $SMe_2$'s as can be accommodated without unfavorable steric interactions. The "fold" region can be seen in Figure 3 to be partly occupied by one $SMe_2$; a second $SMe_2$, bonded to Li(1), in this space would experience some congestion. The absence of a second $SMe_2$ on Li(1) exposes it to a short intermolecular interaction of 2.759 Å to C(22) (at *x*-0.5, 1.5-*y*, *z*-0.5).

**$[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$, 3, and $[Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4]$, 4.** The addition of 3 or more equiv of LiPh to CuBr in $Me_2S$ results in higher order cuprates. The first such species to be crystallized was the complex **3**. X-ray data revealed the first details of the structure of a compound having a $[CuR_3]^{2-}$ ion.[36] Recent experiments have shown that these ions are apparently not formed in ether solutions.[40] One possible reason for this may lie in the structures of the cuprate species themselves. Formation of the higher cuprate probably involves an attack by an extra LiPh on the lower order cuprates $[Li_2Cu_3Ph_6]^-$ or $[Li_2Cu_2Ph_4(SMe_2)_3]$ because these species also apparently exist in solution according to NMR evidence. Obviously, attack of a nucleophile such as $Ph^-$ derived from LiPh is less likely in the case of negatively charged cluster. Thus, a reaction illustrated by can more readily be envisaged than the similar reaction with the $[Li_2Cu_3Ph_6]^-$ cluster. The details of the structure of **3** clearly indicate that it is best represented as a combination of the entities $[CuPh_2]^-$ and $[CuPh_3]^{2-}$ linked by three bridging $Li^+$ ions solvated by $SMe_2$. The structure of $[CuPh_3]^{2-}$ or indeed any $[CuR_3]^{2-}$ moiety had not been hitherto reported. The Cu–C(ipso) distances in $[CuPh_3]^{2-}$ average 2.02 Å, whereas for $[CuPh_2]^-$ they are about 1.93 Å.[34] The former value is consistent with a higher coordination number for Cu, whereas the latter distance is very close to those seen in **2**. Oddly, there is considerable asymmetry in the diagonal Cu–C distances 1.916 Å for C(23) vs 1.942(4) Å for C(29) which is matched by a difference in the Li–C distances 2.409 (8) vs 2.274 (9) Å and the dihedrals between the Cu(2)–C vectors and the C(23) and C(29) planes which are 8° and 21.5°, respectively, since Cu(1) is slightly pyramidal with the Cu apex pointed toward Cu(2) which is bent, 164.6 (2)°, toward Cu(1). However, the Cu⋯Cu distances in both molecules of the asymmetric unit are 3.019 and 3.202 Å. Also, the Cu⋯Cu vectors are far (22°) from perpendicular to the trigonal $C(ipso)_3$ plane. It is also possible to account for the movement of the coppers toward each other in terms of the distortions produced by $Li^+$ coordination. These considerations suggest that there is little interaction of a bonding nature, between the two copper centers.



**2** **5** **3**

Attempts to prepare compounds in which the $[CuPh_3]^{2-}$ unit is the sole copper-containing moiety have been unsuccessful so far. The reasons for this difficulty are not obvious since an attack by LiPh or $Ph^-$ on neutral **3** should be possible. However, a plausible explanation arises from the structure of **3** which suggests that the $Li_2CuPh_3$ moiety apparently readily coordinates another $Li^+$ ion to give the species $[Li_3CuPh_3]^+$. Thus, **3** should be more properly regarded as a combination of the ions $[Li_3CuPh_3]^+$ and $[CuPh_2]^-$ which are bridged by two of the three $Li^+$ ions. The $[Li_3CuPh_3]^+$ moiety can, in fact, be considered as part of the

---

[38] For examples, see: Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Inorg. Chem.* **1981**, *20*, 151 and references therein.

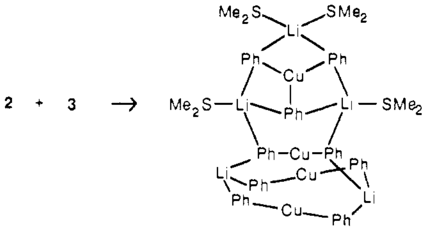
[39] For examples, see: Setzer, W. N., Schleyer, P. R. *Adv. Organomet. Chem.* **1985**, *24*, 354.

[40] Bertz, S. Personal communication.

[41] (a) Lorenzen, N. P.; Weiss, E. *Angew. Chem. Int. Ed. Engl.* **1990**, *102*, 322. (b) Bentz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. Lipschutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032.

structure of both **3** and **4** with either [CuPh$_2$]$^-$ in **3**, or a very weakly associated trimer [Li$_2$Cu$_3$Ph$_6$]$^-$ in **4**, behaving as counter anions. Part of the problem in crystallizing pure Li$_2$CuPh$_3$ may therefore be the lack of available counter anions, that do not contain copper, to cocrystallize with [Li$_3$CuPh$_3$]$^+$. The only other anions that appear to be present in the reaction system, which produced **3** or **4**, are either Br$^-$, most of which is precipitated as LiBr, or Ph$^-$ which is unknown in the free state and in any case would be exceedingly reactive toward the solvent system. It may be that the addition of an appropriate non-copper-containing counter anion may afford the desired product.

The complex **4** was obtained during unsuccessful attempts to obtain a species corresponding to the higher order cuprate formula Li$_2$CuR$_3$. A possible reason why a species, having this formula, was not obtained is given in the preceding paragraph. As already mentioned, the structure of **4** is comprised of two separated entities: one the cation [Li$_3$CuPh$_3$(SMe$_2$)$_4$]$^+$, corresponding very closely to the same species that was observed in **3**, and two, the anion [Li$_2$Cu$_3$Ph$_6$]$^-$, which is related to the species found when LiCuPh$_2$ is crystallized from ether solvents. The assembly of **4** could be regarded as a result of a reaction between **2** and **3** as shown below.



**4**

The formation of the anion [Li$_2$Cu$_3$Ph$_6$]$^-$ in this system, but not in the reaction system that produced **2**, may be accounted for on the basis that Li$_2$CuPh$_3$ again solvates Li$^+$ to give the more symmetric [Li$_3$CuPh$_3$]$^+$ which then can crystallize with the available anions such as [CuPh$_2$]$^-$ in **3** or [Li$_2$Cu$_3$Ph$_6$]$^-$ in **4**, depending on the conditions. Perhaps in this case [Li$_3$CuPh$_3$]$^+$ crystallizes with [Li$_2$Cu$_3$Ph$_6$]$^-$ instead of [CuPh$_2$]$^-$ owing to the slightly different solvent mix (added hexane) or to the slightly more ionic character, >3 equiv, of PhLi. The Li$_2$Cu$_3$ array in **4** is considerably more flattened than it is in the [Li$_2$Cu$_3$Ph$_6$]$^-$ moieties crystallized from Et$_2$O or THF. In **4**, this is reflected in a twisting of the triangles comprised of the two planes of three ipso carbons, relative to each other until they almost define trigonal antiprismatic structure. In the ether crystallized [Li$_2$Cu$_3$Ph$_6$]$^-$ ion the same atoms comprise an almost regular trigonal prism. It is not known at present if the distortions in **4** are due to its interaction with the [Li$_3$CuPh$_3$]$^+$ moiety.

## Conclusions

The results described in this paper show that it is possible to isolate crystals that have the higher order cuprate ion [CuPh$_3$]$^{2-}$ as part of their structure. Moreover, the utility of Me$_2$S solvent in cuprate and in organocopper systems has been confirmed. In addition, it has been demonstrated conclusively that compounds **1–5** form part of a series of compounds which can be interrelated in a logical way. There is, in addition, a close correspondence between the structures crystallized from Me$_2$S and the structures deduced from solution NMR studies. Significantly, it is now apparent that the structure of the lower order cuprate LiCuPh$_2$ in Me$_2$S may be different from its structure in ethers. This difference provides one explanation of why the higher order cuprate forms in Me$_2$S but not readily in ether solvents. Work on these interesting systems is continuing.

**Acknowledgment.** This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF through instrumentation Grant CHE-8802721. M.M.O. acknowledges the guidance and support of R. F. Fenske during her graduate years at the University of Wisconsin.

**Note Added in Proof.** After this work had been carried out a number of papers appeared which described research of considerable relevance. The first concerns the structure of the compound [Li$_2$Cu$_2$Ph$_4$·(Et$_2$O)$_2$][41a] which is very closely related to the structure of **2**. The other papers[41b,c] concerned the structures of higher order cyanocuprates in solution.

**Supplementary Material Available:** Full details of the structure solutions and refinement and tables of atomic coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (27 pages); tables of observed and calculated structure factors (104 pages). Ordering information is given on any current masthead page.