Reaction of 2-(Alkylthiomethyl)phenyllithium with Copper(I) Halides and Structure and Properties of One of the Products —Copper(I) Complexes of 2,2′-Bis(alkylthiomethyl)biphenyl¹⁾

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The title reactions did not afford the corresponding organocopper compound as a stable entity, but rather a dimerized biphenyl compound (2,2′-bis(alkylthiomethyl)biphenyl), its copper(I) halide complex, and alkyl benzyl sulfide. Their yields were influenced by the kind of halides in the copper reagent. The stability and reactivity of the intermediate organocopper compound is discussed on the basis of the ligand-metal interactions. The copper(I) halide complex with the biphenyl which carries two sulfane ligands has a unique polymeric structure in crystals, as evidenced by X-ray analysis, whereas it dissociates into a monomeric form on dissolution in organic solvents. The properties of the complexes were examined by NMR and XPS as well.

Previous studies on various organocopper compounds have demonstrated that intramolecular ligands which could coordinate to the copper atom enhanced the stability of the reactive species, as well as influencing the reactivities.²⁻⁵⁾ Among various ligands, the effect of intramolecular amine ligands is well documented; for example, phenylcopper derivatives, which carry an intramolecular amine ligand such as 2-(dimethylaminomethyl)phenylcopper, are much more stable than the ligand-free compound.⁶⁻¹⁰⁾

In contrast to several examples of the amine-stabilized organocoppers, reports on organocopper compounds bearing an intramolecular sulfane-sulfur ligand are few in spite of the fact that interactions between copper and sulfur atoms are as strong as predicted from the hard and soft acids and bases principle. Indeed, very stable organocopper compounds which carry thiolate ligand(s) have been reported,¹¹⁾ but the only report in the literature on the intramolecular sulfane ligand(s) for coordination to copper is the use of phenylcoppers stabilized by sulfur ligands at the ortho benzylic position¹²⁾ by Ziegler et al. for the cross coupling of aryl groups. Unfortunately, the effect of the intramolecular sulfur ligands on the stability was not clear from their experimental results, since the phenylcopper was reacted with another reagent without isolation.

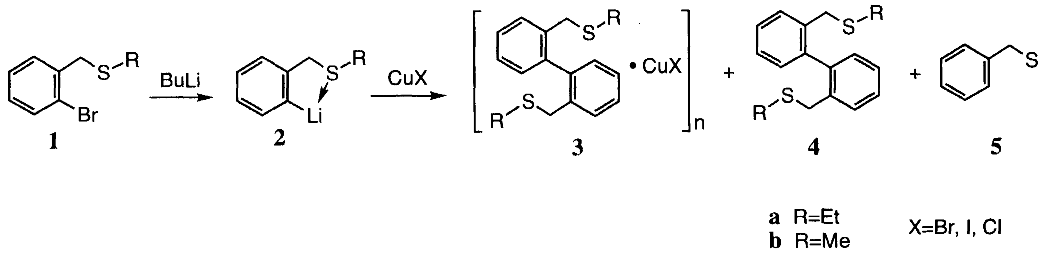
In order to get further insight into the nature of the sulfur-ligand-containing organocopper compounds, we tried to prepare a phenylcopper carrying an alkylthiomethyl group at the ortho position. We had utilized this ligand system for the studies of interaction of the intramolecular sulfane ligand with various metal and metalloids centers.¹³,¹⁴⁾ In an effort to prepare such an organocopper compound, 2-(alkylthiomethyl)phenyllithium was reacted with a copper(I) halide in the usual manner. However, we could not obtain the desired organocopper compound but rather found a dimerized compound, 2,2′-bis(alkylthiomethyl)biphenyl, and a copper halide complex of the biphenyl ligand. This paper reports the results of the reactions and the effect of the intramolecular sulfane-sulfur ligands on the stability and reactivity of organocopper compounds.

The copper halide complex of the difunctional sulfane ligand, one of the products, is an interesting molecule from the standpoint of coordination chemistry because copper(I) ions are able to take a variety of aggregation forms depending on the nature of the ligands.¹⁵⁾ Therefore, the structure and properties of the copper halide complexes were investigated from various aspects including X-ray analysis, molecular weight analysis, and NMR spectroscopy and XPS.

Results and Discussion

Reaction and Product Identification. A solution of 2-(ethylthiomethyl)phenyllithium (**2a**) was prepared by the halogen–lithium exchange method from the corresponding bromide **1a** and butyllithium (Scheme 1). This solution was treated with one equivalent of copper(I) bromide at −30 °C. As the temperature was increased to 0 °C, the color of the solution changed from pale yellow to black, with formation of a dark precipitate. After removal of the insoluble materials, three compounds were isolated as major products: 2,2′-bis(ethylthiomethyl)biphenyl (**4a**), 1 : 1 complex of **4a** with CuBr [**3a** (X = Br)], and benzyl ethyl sulfide (**5a**) in 21, 33, and 13% yields, respectively. The new compounds were characterized as follows.

^{1}H NMR spectrum of compound **4a** showed an AB quartet due to the benzylic methylene protons at ca. 3.5 ppm and a set of ABCD patterns in the aromatic region. Mass analysis suggested the presence of two phenyl units in a



Scheme 1.

molecule. These spectroscopic data support the dimerized biphenyl structure, where the benzylic methylene protons are magnetically nonequivalent, due to the restricted rotation around the biphenyl axis. Compound **4a** was synthesized by an independent route shown in Scheme 2. 2,2′-Bis(bromomethyl)biphenyl (**7**), prepared from diphenoic anhydride (**6**) by reduction followed by bromination,[16)] was treated with sodium ethanethiolate to give an oily material. This product was identical with the compound obtained via the organolithium route.

The structure of **3a** (X = Br) was determined by the X-ray analysis as a CuBr complex of the biphenyl ligand in 1 : 1 ratio. The decomposition of **3a** (X = Br) at high temperature in organic solvents gave CuBr and **4a**. Inversely, the treatment of **4a** with one mole of copper(I) bromide in acetonitrile gave the complex **3a** (X = Br) in a good yield. The analytical and spectroscopic data also support the structure. Structural features and physical properties of the complex are described later.

The reaction of 2-(methylthiomethyl)phenyllithium (**2b**) with CuBr was carried out similarly. As shown in Table 1, the product distribution is almost the same as that of the *S*-ethyl compound. That is, the effect of the alkyl group at the sulfur atom on the reactivities is very small.

Effect of Copper(I) Halide. The reactions were also performed by the use of CuI and CuCl in order to get insight into the effect of copper reagent on the reactivities. The results are listed in Table 1.

The reaction of **2a** with copper(I) iodide gave the CuI complex of the biphenyl ligand in a low yield (6%), as well as **4a** (31%) and **5a** (22%). ^{1}H NMR spectrum of the copper complex **3a** (X = I) has a similar signal pattern as that of the CuBr complex **3a** (X = Br), the chemical shifts being slightly different. The CuI complex could be obtained by the treatment of **4a** with one equivalent of CuI in acetonitrile, as was true for the CuBr complex case. The reaction of the *S*-methyl compound also gave the CuI complex of 2,2′-bis(methylthiomethyl)biphenyl in 17% yield.

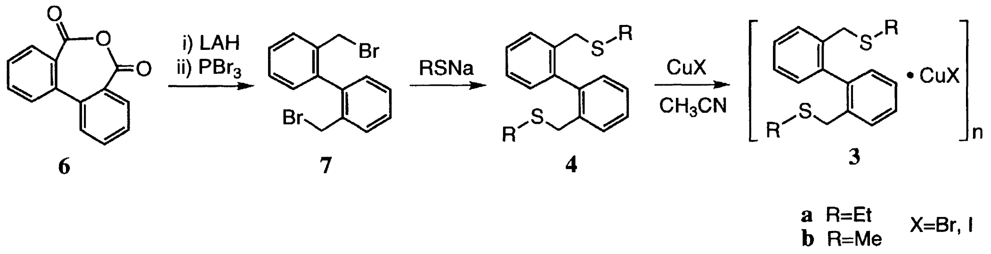
Table 1. Isolated Yields (%) of Products from Reaction of 2-(Alkylthiomethyl)phenyllithium (**2**) and Copper Halide (CuX)

		Products		
Alkyl	X	**3**	**4**	**5**
Et	Br	33	21	13
Et	I	6	31	22
Et	Cl	Trace[a)]	69	10
Me	Br	30	19	4
Me	I	17	30	15
Me	Cl	Trace[a)]	55	4

a) The stoichiometry of CuCl and the ligand could not be determined.

The reaction with copper(I) chloride mainly afforded the biphenyl compound **4** irrespective of the kind of *S*-alkyl groups, ethyl or methyl. Although a small amount of solid product was separated from the reaction mixture, we failed to characterize the product due to its small quantity and difficulty in purification. The treatment of CuCl with the difunctional ligand **4** in acetonitrile gave a solid material, which seemed to be a CuCl complex. However, its composition was dependent on the conditions of the reaction and crystallization, and the decoordination or decomposition took place. These experiments suggest that CuCl has a low ability to form a complex with the difunctional sulfane ligand as a stable form, so that the free biphenyl compound is obtained in high yields.

Nature of Intermediate Organocopper Compound. The reaction of the organolithium compound **2** with one equivalent of copper bromide should initially produce the corresponding organocopper compound, 2-(alkylthiomethyl)phenylcopper(I) (**8**). However, this compound could not be isolated nor spectroscopically detected from the reaction



Scheme 2.

mixture: **8** is not stable enough to survive under the reaction conditions but gives only the decomposition products. Namely, a 2-alkylthiomethyl group at the ortho position has much lower ability for stabilizing the reactive phenylcopper than the corresponding amine ligand, where the phenylcopper is isolable under ambient conditions.[8)] This result is contrary to our expectation that soft sulfur ligands should strongly interact with copper atoms, which are also soft acids, in the same molecule.

In intramolecular coordination compounds, the extent of coordination is affected not only by the affinity between ligands and metals predicted from the general HSAB principle but also by the position and flexibility of the ligand atom. One of the reasons for the instability of **8** is the difficulty in the formation of the five-membered chelation due to the long bond distances involving the sulfur and copper atoms. From the viewpoint of the steric protection, the long C–S bond and the presence of only one substituent at the end of the sulfane ligand, with respect to the short C–N bond and the presence of two substituents in the dialkylamino group, seem to make an alkylthio group inferior relative to a dialkylamino group for stabilization of arylcoppers. These factors reduce the stabilizing ability of 2-(alkylthiomethyl)phenyl group toward organocopper species.

In discussing the stability of organocopper compounds, we must take the aggregation state into consideration, since they usually exist as oligomeric forms in the solid phase and solutions.[2,3,9)] However, the available data provide little information on the effect of the intramolecular ligand on the aggregation state. Further studies should make this point clearer.

Dimerization and hydrolysis are typical fates of reactive organocopper compounds.[2—4,17)] These reactions lead **8** to the biphenyl **4** and alkyl benzyl sulfide **5**, respectively. Thus the produced biphenyl ligand **4**, which can tightly coordinate to copper ions, forms a complex with copper halide to give the complex **3**. The reaction of the organolithium compound with copper halides is reasonably explained by the formation of organocopper compound **8** as a reaction intermediate. The reaction pathway is shown in Scheme 3.

Physical Properties of Copper Halide Complexes 3. The copper halide complexes of 2,2′-(alkylthiomethyl)biphenyls are colorless crystals and soluble in ordinary polar organic solvents, even though the solubility is not so high. Although the complexes are stable in solution at room temperature, decoordination takes place at higher temperatures: The heating of **3a** (X = Br) in toluene at reflux gave a white solid, CuBr, within 10 min and the free biphenyl ligand was recovered from the supernatant.

As mentioned in the next section, the complexes take polymeric structures in crystals. Therefore, it is natural that molecules dissociate into smaller pieces on dissolution in organic solvents. In order to investigate the aggregation state of the complexes in solution, molecular weights were measured by the vapor pressure osmometric method. The observed values were 437±20 and 424±20 for compounds **3a** (X = Br) and **3b** (X = Br), respectively, for chloroform solutions.

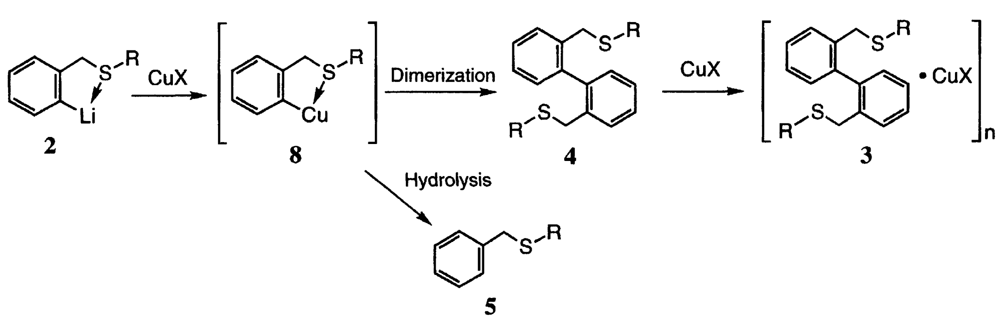
These molecular weights are nearly equal to the total weight of one difunctional ligand and one copper bromide. This suggests that molecules dissociate into a monomeric state in solutions. Namely, they exist in pairs of the biphenyl ligand and the copper bromide species. The crystalline complex was quantitatively reproduced by the evaporation of the solvent. In other words, the biphenyl ligands were again assembled by the coordination to copper(I) ions. Therefore, the aggregation states of the complexes are interconverted between polymeric and monomeric structures by the dissolution and crystallization.

The electronic state of the atoms involved in the copper halide complexes in the solid state was investigated by X-ray photoelectron spectroscopy (XPS). The binding energies of Cu $2p_{3/2}$, S 2p, I $3d_{5/2}$, and Br 3d electrons for compounds **3a** (X = Br and I) are listed in Table 2, together with those of the ligand-free copper halides.

The copper bands appear at ca. 933.5 eV for all the materials, this value being typical for copper atoms at oxidation state +1.[18,19)] The coordination of the difunctional biphenyl ligand hardly influences the binding energy of the copper atoms in either the CuBr or the CuI complexes. On the other

Table 2. XPS Data of Copper Halide Complexes of 2,2′-Bis(ethylthiomethyl)biphenyl (**3a**) and Free Copper Halides

	Binding energy/eV (half height width/eV)			
Compound	Cu $2p_{3/2}$	S 2p	I $3d_{5/2}$	Br 3d
3a (X = Br)	933.6 (2.1)	164.0 (2.5)	—	70.0 (2.4)
CuBr	933.3 (1.7)	—	—	70.8 (1.6)
3a (X = I)	933.5 (2.1)	164.0 (2.7)	619.8 (2.0)	—
CuI	933.7 (1.6)	—	620.0 (1.4)	—



Scheme 3.

hand, the line width of the copper band is apparently larger for the complex than for the ligand-free copper salt. This line broadening is attributable to complex formation with the sulfur ligand. This tendency is also noticed for the I $3d_{5/2}$ and Br 3d bands in the CuI and CuBr complexes, respectively.

NMR Spectra of Complexes 3. ^{1}H NMR signals due to the benzylic methylene and ethyl protons in compound **3a** (X=Br) were observed as an AB quartet and an ABX_3 pattern, respectively, in $CDCl_3$ at room temperature. The chemical shifts of the benzylic and the ethyl methylene protons are at lower fields by 0.29 and 0.39 ppm than those for the metal-free ligand, respectively. The ^{13}C signals due to the benzylic carbon and the ethyl-methylene carbon are also deshielded by 1.7 and 4.2 ppm, respectively. As for the *S*-methyl complex **3b** (X = Br), the signal due to the *S*-methyl protons was shifted downfield by 0.38 ppm by the complex formation with CuBr. The downfield shifts are less significant for the CuI complexes.

The downfield shift of the chemical shifts is mainly attributed to the coordination of the sulfur atoms to the copper atom; these phenomena were observed for other coordination compounds of similar structures.[9,13,20] The conformational change in the biphenyl moiety caused by the complexation can also affect the chemical shifts of the proton and carbon atoms by the ring current effect, but its contribution is not clear from the available data.

^{1}H NMR signals of **3a** (X = Br) showed no line shape changes in the temperature range from room temperature to 75 °C in toluene-d_8. At higher temperatures, the complex decomposed with broadenings of the signals which were drifting, this being a result of decoordination of copper salt. A similar phenomenon was observed when chlorobenzene-d_5 or nitrobenzene-d_5 was used as solvent. This observation indicates that dynamic processes which exchange the magnetic sites of the diastereotopic pair are very slow on the NMR time scale even at 75 °C, its barrier being at least 20 kcal mol^{-1} (1 cal = 4.184 J).

The barrier to C–C bond rotation in biphenyls that carry a methyl or a substituent of an equivalent size at 2 and 2′ positions is ca. 20 kcal mol^{-1}.[21,22] The nonequivalence of the benzylic methylene protons in the ^{1}H NMR spectra of **4** is in conformity with the barrier height. Because the conformational change of the biphenyl moiety in complex **3** is furthermore restricted by the coordination to copper atoms, the rotational barrier should be higher than that in the metal free ligand, unless the reversible decoordination takes place very fast in solutions.

The inversion at the coordinated sulfur atoms is another process which may influence the NMR line shapes at various temperatures. Unfortunately, there are no reports on the kinetic parameters of the sulfur inversion in copper-sulfur complexes to our knowledge.[23] Recently, we reported the barrier to sulfur inversion in gold–sulfane complexes by means of the dynamic NMR method and MO calculation: about 14 kcal mol^{-1} for gold(I) chloride–dialkyl sulfide complexes.[20] The calculation predicts that CuCl–SMe_2 complex has a lower barrier to sulfur inversion than the AuCl complex. Therefore, the inversion barrier in the copper complexes is expected to be lower than 14 kcal mol^{-1}.

In order to obtain more direct evidence for the inversion barrier, ^{1}H NMR spectra of a model compound, copper bromide complex of diethyl sulfide,[24] were measured in acetonitrile-d_3 at various temperatures. The signal due to the methylene protons appeared as a quartet at room temperature, whereas the signal became broad to some extent at −50 °C. If this line shape change is ascribed to the slow sulfur inversion, the barrier can be estimated to be ca. 11 kcal mol^{-1}. These results enable us to conclude that the sulfur inversion in complex **3** takes place much faster than the NMR time scale at room temperature or higher temperatures and the nonequivalence of the methylene protons is attributed to the chirality about the axis of the biphenyl moiety.

X-Ray Structure of Complexes 3. The molecular structure of compound **3a** (X = Br) was analyzed by X-ray crystallography. Final positional and thermal parameters are listed in Table 3 and selected positional parameters in Table 4. An ORTEP drawing of an asymmetric unit is shown in Fig. 1 and a perspective view of the infinite sequence in Fig. 2.

The structure has a repeating unit made of two molecules of the biphenyl ligand **4a** with a dinuclear copper center, with two bridging bromine atoms to form a polymeric structure in crystals. The infinite sequence is formed by copper atoms that take one sulfur of one biphenyl molecule and another sulfur from another biphenyl molecule. Another copper atom (Cu′) in the core takes another pair of compounds **4a** as a

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in [2,2′-Bis(ethylthiomethyl)biphenyl]bromocopper(I) [**3a** (X = Br)][a)]

Atom	*x*	*y*	*z*	B_{eq}[b)]
Cu	0.08876(7)	−0.04856(5)	1.0688(1)	3.88(2)
Br	−0.11915(6)	−0.04846(4)	1.10572(9)	3.93(2)
S(1)	0.1021(2)	−0.13057(9)	0.8855(2)	3.34(5)
S(2)	0.2163(1)	−0.03352(9)	0.3265(2)	3.62(5)
C(1)	0.3474(6)	−0.1372(3)	0.7385(10)	3.0(2)
C(2)	0.3397(6)	−0.1393(3)	0.9061(9)	3.1(2)
C(3)	0.4257(8)	−0.1082(4)	1.025(1)	4.3(2)
C(4)	0.5174(8)	−0.0770(4)	0.985(1)	5.1(3)
C(5)	0.5232(7)	−0.0729(4)	0.819(2)	5.2(3)
C(6)	0.4394(7)	−0.1031(4)	0.696(1)	4.1(2)
C(7)	0.2644(6)	−0.1739(3)	0.6052(9)	3.2(2)
C(8)	0.1736(6)	−0.1454(3)	0.4865(9)	3.1(2)
C(9)	0.0987(7)	−0.1829(4)	0.367(1)	4.3(2)
C(10)	0.1114(8)	−0.2493(4)	0.366(1)	4.8(3)
C(11)	0.2008(7)	−0.2786(3)	0.480(1)	4.4(2)
C(12)	0.2756(6)	−0.2413(4)	0.5985(9)	4.0(2)
C(13)	0.2408(6)	−0.1742(3)	0.9557(9)	3.7(2)
C(14)	−0.0041(6)	−0.1925(3)	0.9069(10)	4.4(2)
C(15)	−0.0283(8)	−0.2402(4)	0.766(1)	9.0(3)
C(16)	0.1510(8)	−0.0734(4)	0.4853(10)	3.7(2)
C(17)	0.1927(8)	0.0511(4)	0.3750(10)	4.8(2)
C(18)	0.281(1)	0.0739(7)	0.530(2)	8.0(4)

a) Values in parentheses are estimated standard deviations.

b) $B_{eq}/\text{Å}^2 = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 4. Selected Structural Parameters in [2,2′-Bis(ethylthiomethyl)biphenyl]bromocopper(I) [**3a** (X = Br)][a)]

Bond distances (Å)			
Cu–Br	2.499(1)	Cu–Br′	2.536(1)
Cu–S(1)	2.295(2)	Cu–S(2)′	2.304(2)
Bond angles (°)			
Br–Cu–Br′	109.17(4)	Br–Cu–S(1)	106.82(6)
Br–Cu–S(2)′	109.14(6)	Br′–Cu–S(1)	100.49(6)
Br′–Cu–S(2)′	105.31(6)	S(1)–Cu–S(2)′	124.91(8)
Cu–Br–Cu′	70.83(4)		
Torsion angle (°)[b)]			
C(2)–C(1)–C(7)–C(8)	106.3(8)		

a) Values in parentheses are estimated standard deviations. Atoms with ′ mean those generated by a symmetric operation from the original molecule. b) Values for the biphenyl unit with *P* stereochemistry.

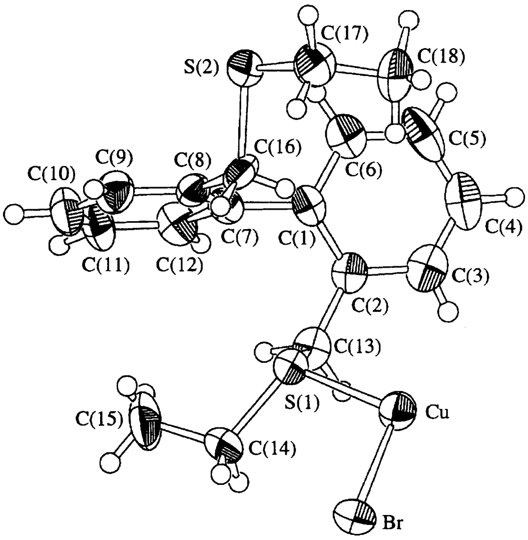


Fig. 1. ORTEP drawing of compound **3a** (X = Br) for an asymmetric unit with thermal ellipsoids at 50% probability.

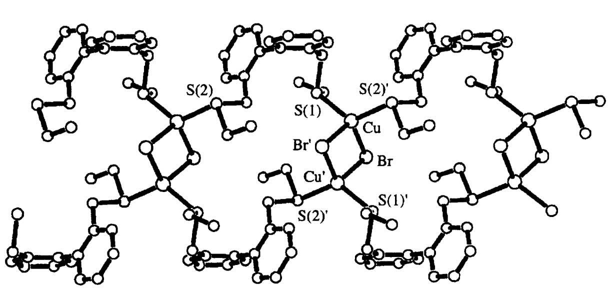


Fig. 2. Polymeric structure of compound **3a** (X = Br).

ligand at the opposite side. Such a linkage constructs a kind of infinite strand of the biphenyl ligands at both sides of the copper centers.

The Cu_2Br_2 center has a planar parallelogram geometry, where the two copper atoms are at the apexes that form obtuse angles (109.17°) and the two halogens at the apexes that form acute angles (70.83°). In this geometry, Cu–Br bonds have two lengths of 2.499 and 2.536 Å, the latter being longer by 0.04 Å. The distance between the two copper atoms in a dinuclear center is 2.918 Å. These structural parameters are in the range of standard values for copper(I) dinuclear complexes with two bromine bridges.[15)]

The copper atom takes a distorted tetrahedral geometry with two bromine atoms and two sulfur ligands. The largest value among the bond angles at the copper atom is the S–Cu–S angle, 124.9°. The Cu–S bond lengths of about 2.30 Å are usual for that in a copper(I) complex with terminal sulfide ligands.[15)]

In the biphenyl molecules, the two benzene rings are nearly orthogonal to each other, as judged from the C(2)–C(1)–C(7)–C(8) torsion angle of 106.3°. This conformation allows the biphenyl molecules to take two enantiomeric forms about the C(1)–C(7) axis: *P* and *M* stereochemistries. In the structure shown in Fig. 2, biphenyl ligands with *P*- and *M*-helixes are regularly arranged along lower and upper rows, respectively. In crystals, the biphenyl difunctional ligands are assembled with the aid of copper(I) ions under the perfect control of the geometry including the stereochemistry, to form a unique polymeric structure.

Experimental

^{1}H NMR spectra were measured on a Varian Gemini-300 or a JEOL GSX-400 spectrometer operating at 300.1 and 399.8 MHz, respectively. Spectra at various temperatures were measured on the 400 MHz spectrometer. Mass spectra were measured by a JEOL JMS-DX303 spectrometer by the electron impact method. Melting points are uncorrected. Elemental analyses were performed by a Perkin–Elmer 240C analyzer. XPS spectra were collected on a Shimadzu ESCA850 spectrometer with Mg *Kα* radiation and the binding energies were referred to C 1s signal at 285.0 eV. Molecular weight was measured by the vapor pressure osmometric method using a CORONA 117 molecular weight apparatus for chloroform solutions at 40 °C.

1-Bromo-2-(methylthiomethyl)benzene[25)] and 1-bromo-2-(ethylthiomethyl)benzene[26)] were prepared from 1-bromo-2-(bromomethyl)benzene and a sodium alkylthiolate by the known methods.

Reaction of 2-(Ethylthiomethyl)phenyllithium with Copper(I) Bromide. To a solution of 1-bromo-2-(ethylthiomethyl)benzene (2.00 g or 9.21 mmol) in 20 mL of dry ether was added 6.5 mL (10.1 mmol) of a 15% hexane solution of butyllithium at −78 °C under a nitrogen atmosphere. After the solution was stirred for 2 h at −30 °C, 1.32 g (9.21 mmol) of CuBr was added in small portions. The reaction mixture was warmed up to 0 °C and stirred for 3 h. The dark precipitates were removed by filtration and washed with diethyl ether followed by dichloromethane. The filtrate was evaporated and the residue was extracted with dichloromethane to remove lithium bromide. Recrystallization of the extracts with hexane-dichloromethane gave 0.64 g (33%) of colorless crystals, [2,2′-bis(ethylthiomethyl)biphenyl]bromocopper(I). From the filtrate of the recrystallization, 0.29 g (21%) of 2,2′-bis(ethylthiomethyl)biphenyl and 0.18 g (13%) of benzyl ethyl sulfide were isolated by chromatography on silica gel (eluent hexane), both compounds giving ^{1}H NMR spectra identical with those of the authentic specimens.

[2,2′-Bis(ethylthiomethyl)biphenyl]bromocopper(I) [3a (X = Br)]. Mp 147—148 °C. Found: C, 48.57; H, 4.94%. Calcd for $C_{18}H_{22}BrCuS_2$: C, 48.48; H, 4.97%. ^{1}H NMR (CDCl$_3$) $\delta = 1.27$ (6H, t, X of ABX$_3$, $J = 7.5$ Hz), 2.71 and 2.76 (4H, AB of ABX$_3$,

J_{AB} = 13.3, J_{AX} = J_{BX} = 7.5 Hz), 3.69 and 3.86 (4H, ABq, J = 11.8 Hz), 7.13 (2H, dd, J = 1.4 and 7.5 Hz), 7.32 (2H, dt, J = 1.4 and 7.4 Hz), 7.38 (2H, dt, J = 1.4 and 7.5 Hz), 7.53 (2H, dd, J = 1.4 and 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 13.9, 30.1, 35.3, 127.2, 128.1, 130.5, 131.1, 134.6, 139.8.

Reaction of 2-(Ethylthiomethyl)phenyllithium with Copper(I) Iodide. The reaction was similarly performed. The product yields are shown in Table 1.

[2,2′-Bis(ethylthiomethyl)biphenyl]iodocopper(I) [3a (X = I)]. Mp 135—136 °C. Found: C, 42.78; H, 4.27%. Calcd for $C_{18}H_{22}CuIS_2$: C, 42.44; H, 4.35%. ^{1}H NMR ($CDCl_3$) δ = 1.20 (6H, t, J = 7.4 Hz), 2.42—2.63 (4H, m), 3.59 and 3.83 (4H, ABq, J = 12.2 Hz), 7.13 (2H, dd, J = 1.5 and 7.4 Hz), 7.28 (2H, dt, J = 1.6 and 7.4 Hz), 7.34 (2H, dt, J = 1.7 and 7.4 Hz), 7.57 (2H, d, J = 7.7 Hz).

Reaction of 2-(Ethylthiomethyl)phenyllithium with Copper(I) Chloride. The reaction was similarly performed. The yields of the products are given in Table 1. Although a small amount of solid material (less than 3%) was formed, it could not be made pure, because CuCl tended to be lost from the compound on crystallization.

Reaction of 2-(Methylthiomethyl)phenyllithium with Copper(I) Halides. These reactions were similarly performed as the reaction of the 2-(ethylthiomethyl)phenyllithium. The results are given in Table 1. Identification of compounds other than those described below was performed by comparing the ^{1}H NMR spectra with the authentic specimens.

[2, 2′- Bis(methylthiomethyl)biphenyl]bromocopper(I) [3b (X = Br)]. Mp 162—163 °C. Found: C, 45.89; H, 4.13%. Calcd for $C_{16}H_{18}BrCuS_2$: C, 45.99; H, 4.34%. ^{1}H NMR ($CDCl_3$) δ = 2.32 (6H, s), 3.65 and 3.92 (4H, ABq, J = 12.2 Hz), 7.12 (2H, dd, J = 1.4 and 7.4 Hz), 7.33 (2H, dd, J = 1.7 and 7.5 Hz), 7.39 (2H, dd, J = 1.7 and 7.5 Hz), 7.51 (2H, dd, J = 1.6 and 7.6 Hz).

[2, 2′- Bis(methylthiomethyl)biphenyl]iodocopper(I) [3b (X = I)]. Mp 149—151 °C. Found: C, 41.30; H, 3.81%. Calcd for $C_{16}H_{18}CuIS_2$: C, 41.34; H, 3.90%. ^{1}H NMR ($CDCl_3$) δ = 2.04 (6H, s), 3.52 (2H, d, J=12.7 Hz), 3.77 (2H, br), 7.13 (2H, dd, J = 1.4 and 7.4 Hz), 7.28 (2H, dt, J = 1.4 and 7.4 Hz), 7.34 (2H, dt, J = 1.6 and 7.4 Hz), 7.54 (2H, d, J = 7.2 Hz).

Independent Synthesis of 2,2′-Bis(ethylthiomethyl)biphenyl (4a). To a solution of 2.7 g (63 mmol) of sodium hydroxide in 80 mL of methanol was slowly added 3.8 mL (63 mmol) of ethanethiol. To this solution was added 7.7 g (23 mmol) of 2, 2′-bis(bromomethyl)biphenyl$^{16)}$ and the mixture was stirred for 2 h at room temperature. After addition of 50 mL of water, the reaction mixture was extracted with dichloromethane. The organic layer was separated and washed with aqueous sodium hydroxide, followed by aqueous sodium chloride. The solution was dried over magnesium sulfate and the solvent was evaporated. Distillation of the residue under a reduced pressure gave 5.1 g (81%) of the desired compound as colorless liquid, which boiled at 155—160 °C/0.3 mmHg (1 mmHg = 133.322 Pa). Found: C, 71.26; H, 7.46%; M$^+$ 302. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33%; M 302. ^{1}H NMR ($CDCl_3$) δ = 1.08 (6H, t, J = 7.4 Hz), 2.35 (4H, q, J = 7.4 Hz), 3.44 and 3.54 (4H, ABq, J = 13.2 Hz), 7.21 (2H, dd, J = 7.4 and 1.7 Hz), 7.26 (2H, dt, J = 1.5 and 7.4 Hz), 7.33 (2H, dt, J = 1.7 and 7.4 Hz), 7.48 (2H, dd, J = 1.4 and 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.4, 25.9, 33.6, 126.4, 127.6, 129.4, 130.2, 136.5, 140.1.

2,2′-Bis(methylthiomethyl)biphenyl (4b). This compound was similarly prepared. Bp 153—156 °C/0.1 mmHg. Found: C, 70.31; H, 6.51%; M$^+$ 274. Calcd for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61%; M 274. ^{1}H NMR ($CDCl_3$) δ = 1.94 (6H, s), 3.40 and 3.51 (4H, ABq, J=13.3 Hz), 7.20 (2H, dd, J = 1.7 and 7.4 Hz), 7.29 (2H, dt, J = 1.6 and 7.4 Hz), 7.35 (2H, dt, J = 1.7 and 7.3 Hz), 7.47 (2H, dd, J = 1.5 and 7.6 Hz).

Reaction of 2,2′-Bis(alkylthiomethyl)biphenyl with Copper(I) Halides. To a solution of 0.50 mmol of a 2,2′-bis(alkylthiomethyl)biphenyl in 3 mL of acetonitrile was added a solution of 0.50 mmol of CuBr or CuI in 3 mL of acetonitrile with stirring at room temperature. The white precipitates were separated and recrystallized from dichloromethane. All compounds showed the physical properties identical with those of the copper complex obtained in the organolithium route.

^{1}H NMR Measurement of CuBr–Diethyl Sulfide Complex. The complex was prepared from copper bromide and diethyl sulfide by the known method.$^{24)}$ The sample for the NMR measurement was made on a solution prepared by the dissolution of about 10 mg of the complex in 0.6 mL of acetonitrile-d_3 in an NMR sample tube. The measurements were performed by the 400 MHz NMR spectrometer. ^{1}H NMR (CD_3CN, r.t.) δ = 1.20 (6H, t, J = 7.3 Hz), 2.58 (4H, q, J = 7.3 Hz). The signal at δ = 2.58 became broad at −50 °C.

X-Ray Crystallography.$^{27)}$ A single crystal of **3a** (X = Br) used for the measurement was grown from a dichloromethane solution; its size was $0.45 \times 0.20 \times 0.15$ mm^3. Reflection data were collected on a MAC Science MXC18 four circle diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å). The scan mode was a combination of the 2θ method ($2\theta < 30°$) and the ω–2θ method ($2\theta > 30°$). The scan rate was 6° min^{-1} and the scan range was calculated by $1.13° + 0.35° \tan\theta$. The structure was solved by the direct method and refined by the full-matrix least-squares method by using a TEXSAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic parameters for hydrogens. No absorption correction was employed. The total number of measured unique reflection was 5445 within the range of $2° < 2\theta < 60°$ and 2266 reflections within $I > 4\sigma(I)$ were used for the structure determination and refinement. The reflection data were corrected for the Lorentz and polarization effects and secondary extinction. The function minimized was $\sum[w(|F_o| - |F_c|)^2]$, where $w = [\sigma_c^2|F_o|]^{-1}$. Formula $C_{18}H_{22}BrCuS_2$, F.W. 445.95, Monoclinic, Space group $P2_1/n$, a = 11.610(4), b = 20.735(7), c = 8.171(3) Å, β = 103.10(3)°, V = 1915(1) Å^3, Z = 4, D_c = 1.546 g cm^{-3}, μ = 34.44 cm^{-1}, R = 0.047, R_w = 0.032.

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References

1) A preliminary communication: S. Toyota, Y. Matsuda, M. Ōki, and H. Akashi, *Chem. Lett.*, **1995**, 31.

2) A. E. Jukes, *Adv. Organomet. Chem.*, **12**, 215 (1974).

3) G. van Koten and J. G. Noltes, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. A. G. Stone, and E. W. Abel, Pergamon Press, Oxford (1984), Vol. 2, Chap. 14.

4) B. H. Lipshutz and S. Sengupta, *Org. React.*, **41**, 135 (1992).

5) "Organocopper Reagents," ed by R. J. K. Taylor, Oxford University Press, Oxford (1994).

6) G. van Koten, A. J. Leusink, and J. G. Noltes, *J. Chem. Soc.*,

Chem. Commn., **1970**, 1107.

7) G. van Koten, A. J. Leusink, and J. G. Noltes, *Inorg. Nucl. Chem. Lett.*, **7**, 227 (1971).

8) G. van Koten, A. J. Leusink, and J. G. Noltes, *J. Organomet. Chem.*, **84**, 117 (1975).

9) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **84**, 129 (1975).

10) G. van Koten and J. T. B. H. Jastrzebski, *Tetrahedron*, **45**, 569 (1989).

11) D. M. Knotter, D. M. Grove, W. J. J. Smeets, A. L. Spek, and G. van Koten, *J. Am. Chem. Soc.*, **114**, 3400 (1992).

12) F. E. Ziegler, I. Chliwner, K. W. Fowler, S. J. Kanfer, S. J. Kuo, and N. D. Sinha, *J. Am. Chem. Soc.*, **102**, 790 (1980).

13) M. Ōki and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **61**, 1191 (1988).

14) S. Toyota and M. Ōki, *Bull. Chem. Soc. Jpn.*, **64**, 1563 (1991).

15) B. J. Hathaway, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Pergamon Press, Oxford (1987), Vol. 5, Chap. 53.

16) L. M. Tolbert and M. Zaki Ali, *J. Org. Chem.*, **47**, 4793 (1982).

17) H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966).

18) R. R. Gagné, J. L. Allison, C. A. Koval, W. S. Mialki, T. J. Smith, and R. A. Walton, *J. Am. Chem. Soc.*, **102**, 1905 (1980).

19) R. A. Walton, *Inorg. Chem.*, **19**, 1101 (1980).

20) S. Toyota and M. Ōki, *Bull. Chem. Soc. Jpn.*, **68**, 1345 (1995).

21) L. W. Meyer and R. B. Meyer, *J. Am. Chem. Soc.*, **85**, 2170 (1963).

22) G. Bott, L. D. Field, and S. Sternhell, *J. Am. Chem. Soc.*, **102**, 5618 (1980).

23) E. A. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, **32**, 1 (1984).

24) J. San Filippo, Jr., L. E. Zyontz, and J. Potenza, *Inorg. Chem.*, **14**, 1667 (1975).

25) R. Breslow, S. Garratt, L. Kaplan, and D. LaFollette, *J. Am. Chem. Soc.*, **90**, 4051 (1968).

26) G. Bähr and K.-H. Thiele, *Chem. Ber.*, **90**, 1578 (1957).

27) Tables of coordinates for the hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, complete $F_o - F_c$ data, all bond distances and angles, and torsion angles are deposited as Document No. 69065 at the Office of the Editor of Bull. Chem. Soc. Jpn.