2,4-Diphenyl-1-buten-3-yne (5c):[50,51] 5.74 (d, $J_{\text{H-H}}$ = 1.4 Hz), 5.68 (d, $J_{\text{H-H}}$ = 1.4 Hz); M$^+$ = 204.

2,4-Di(*p*-methoxyphenyl)-1-buten-3-yne (5d):[50,51] 5.79 (d, $J_{\text{H-H}}$ = 1.4 Hz), 5.75 (d, $J_{\text{H-H}}$ = 1.4 Hz); M$^+$ = 264.

1-(*p*-Methoxyphenyl)-3-methylenenonyne (5e):[52] 5.05 (s), 5.23 (s).

Anti addition in the case of formation of compound 3 was determined on the basis of the ^{1}H NMR spectra of compounds derived from C$_6$D$_6$. Photochemical experiments and quantum yield determinations were done by using apparatus previously described;[13] all photochemical reactions were maintained at 50 °C in a Pyrex oil bath. Typically, an Oriel focused beam system with a 500-W high-pressure Hg arc lamp was used as a light source.

A Corning CS 0-52 filter was used to transmit wavelengths >350 nm, corresponding to the lowest energy absorption band in the spectrum of 1, which has been assigned previously.[53] For photokinetic experiments, benzene solutions (2.0 mL) of 1 (2.0 mM) and alkyne (100 mM, unless stated otherwise) were used. Crossover experiments were done in a 2:1 mixture of C$_6$D$_6$:C$_6$H$_6$ with aliquots removed from the solution as the reaction progressed. These aliquots were analyzed by GC–MS and compared to standard samples derived from pure C$_6$D$_6$ and C$_6$H$_6$. Crossover experiments were typically allowed to proceed to <10% completion, as H/D exchange with the alkyne substrate was observed after extended periods. Thermal reactions were carried out in a thermostatically controlled bath.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the Rutgers University Research Council is gratefully acknowledged. A.S.G. thanks the Camille and Henry Dreyfus Foundation for a Distinguished New Faculty Grant. We thank Johnson-Matthey for generous loans of rhodium trichloride. Professors P. J. Desrosiers and J. A. Maguire are thanked for helpful discussions.

---

(52) The assignments of the vinyl protons were made on the basis of NOE experiments similar to those described earlier, using the perproteo compound. When the allylic protons (δ 2.10 ppm) were irradiated, a 3.1% enhancement for the vinyl resonance at δ 5.05 ppm was observed; we therefore assign this as cis to the *n*-hexyl group. When the protons of the *p*-methoxyphenyl group (δ 7.01 ppm) were irradiated, a 2.8% enhancement was observed for the other vinyl resonance at δ 5.23 ppm; we therefore assign this as cis to the *p*-methoxyphenyl group.

(53) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485–1488.

Use of Dimethyl Sulfide in Organocopper Chemistry: X-ray Crystal Structures of *cyclo*-Tetrakis(μ-2-methylphenyl)bis(dimethyl sulfide)tetracopper(I) and of the Polymeric Copper Bromide Adduct Bromo(dimethyl sulfide)copper(I)

Bernd Lenders,[†] David M. Grove,[†] Wilberth J. J. Smeets,[‡] Paul van der Sluis,[‡] Anthony L. Spek,[‡]
and Gerard van Koten*,[†]

Department of Metal-Mediated Synthesis, Debye Research Institute, and Laboratory of Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received April 20, 1990

The structure of the 1:1 copper(I) bromide–dimethyl sulfide adduct ([CuBr(SMe$_2$)]) consists of a layered polymeric network. The compound crystallizes in space group $P2_1/c$ (Z = 4), a = 7.161 (1) Å, b = 6.636 (1) Å, c = 11.039 (1) Å, β = 93.92 (1)°, and its X-ray structure was refined to R = 0.021 for 1225 reflections ($I > 2.5\sigma(I)$). The preparation of [Cu$_4$(C$_6$H$_4$Me-2)$_4$(SMe$_2$)$_2$] is described; the compound crystallizes in the tetragonal space group $P4_2$ (Z = 2), a = b = 14.595 (2) Å, c = 7.513 (1) Å, and its X-ray structure was refined to R = 0.025 for 2355 reflections. The crystal structure of [Cu$_4$(C$_6$H$_4$Me-2)$_4$(SMe$_2$)$_2$] comprises discrete tetranuclear clusters having a virtually planar "flattened butterfly" Cu$_4$ core. Adjacent copper atoms are three-center two-electron bridge-bonded by a C$_{\text{ipso}}$ atom of one *o*-tolyl group (Cu⋯Cu 2.4126 (5) and 2.4626 (5) Å) with two nonadjacent copper atoms each being further bonded to the sulfur atom of a coordinating dimethyl sulfide; i.e., there are two two-coordinate and two three-coordinate Cu(I) sites. The cluster exists in two stereoisomeric forms; one form having all the *o*-tolyl methyl groups on the same side of the Cu$_4$ core and a second in which these methyl groups are alternately orientated above and below this core. Variable-temperature ^{1}H and ^{13}C NMR spectra provide evidence for fluxionality and interconversion of various tetranuclear species in solution.

Introduction

The copper bromide reagent [CuBr(SMe$_2$)] has gained a pivotal position as the starting compound for the preparation of cuprates,[1-3] and although it is insoluble in most solvents, it does dissolve in pure dimethyl sulfide (DMS) and in organic solvents to which DMS has been added. Studies of other copper salt–Lewis base adducts with a 1:1 stoichiometry have shown that they can crystallize either in the cubane cluster form (e.g., [CuI(PEt$_3$)]^4 and [CuI(AsEt$_3$)]^4) or with a "step" skeleton (e.g., [CuBr(PPh$_3$)]^5).

[†] Department of Metal-Mediated Synthesis, Debye Research Institute.

[‡] Laboratory of Crystal and Structural Chemistry.

(1) House, H. O.; Chu, C.-Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.

(2) Lipshutz, B. H.; Whitney, S.; Kozlowski, J. A.; Breneman, C. M. *Tetrahedron Lett.* **1986**, *27*, 4273.

(3) Bertz, S. H.; Gibson, C. P.; Dabbagh, G. *Organometallics* **1988**, *7*, 227.

(4) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899.

0276-7333/91/2310-0786$02.50/0

In contrast, the 4:3 adduct of copper iodide with diethyl sulfide ([$Cu_4I_4(SEt_2)_3$]) forms crystals with a polymeric chain structure.[6] A review that includes copper salt adducts has appeared recently.[7]

For the synthesis of organocopper compounds, the use of a soluble copper(I) reagent can have several advantages. In particular, its use may prevent the formation of organocopper–copper(I) salt complexes, which either are insoluble, and therefore do not react further, or are less stable than the organocopper compound and decompose during the synthesis. In the literature, there is no report of the use of either copper halide dimethyl sulfide complexes or DMS as a solvent in the preparation of pure organocopper compounds. We anticipated that in such syntheses the presence of DMS should both improve the solubility of the copper(I) salt reagent and also aid the stabilization of intermediate or transient organocopper species by its coordination to unsaturated copper sites. In addition to the study of these synthetic aspects of DMS usage, we also wish to explore the ligand coordination properties of DMS in organocopper chemistry.

To these ends, we have investigated the synthesis of *o*-tolylcopper from [$CuBr(SMe_2)$] and *o*-tolyllithium. It is well-established that arylcopper compounds have polynuclear structures in which the aryl groups bridge between the copper atoms with multicenter bonds and have the aryl nucleus orientated perpendicular to the Cu···Cu axis.[8,9] These features make a study of the stereochemistry of *o*-tolylcopper very interesting since the presence of the *o*-methyl group can give rise to stereoisomeric polynuclear structures due to different possible orientational combinations of the *o*-tolyl methyl groups with respect to the central copper core. In a recent publication, the stereochemistry and structural aspects of chiral arylcopper compounds have been discussed.[10]

This paper describes the polymeric solid-state structure of [$CuBr(SMe_2)$] and the use of this 1:1 adduct for the preparation of [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$]. The crystal structure of this organocopper compound contains discrete tetranuclear clusters occurring in two stereoisomeric forms; one isomeric form has all *o*-tolyl methyl groups on the same side of the Cu_4 core, whereas the second form has these methyl groups alternately orientated above and below this core.

Experimental Section

General Details. [$CuBr(SMe_2)$] was prepared according to a literature procedure.[1] The preparation of [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$] was performed under dry nitrogen in conventional Schlenk glassware. ^1H NMR spectra were recorded on a Bruker AC 200 P. Chemical shifts are given in ppm (positive to high frequency) relative to Me_4Si.

Procedures. [$Li(C_6H_4Me\text{-}2)$]$_n$. In 30 mL of hexane was dissolved 4.86 g of 2-iodotoluene (22.3 mmol) and to this stirred solution was added dropwise 10 mL of 1.6 M LiBu/hexane (80 mmol) at room temperature. The first drops caused the color of the solution to change to orange. During the addition of the remaining LiBu (ca. 5 min), this color disappeared and [$Li(C_6H_4Me\text{-}2)$]$_n$ precipitated. After centrifugation, the solvent was removed by decantation. The white solid compound was washed three times with 50-mL portions of pentane and dried in vacuo to afford the product as a pyrophoric white powder. *Comment*: Less than the stoichiometric amount of LiBu is used to avoid the formation of lithium compounds that contain the butyl anion and that could give rise to the formation of [CuBu]$_n$ in subsequent reactions.

Table I. Crystal Data for [$CuBr(SMe_2)$] and [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$]

formula	C_2H_6BrCuS	$C_{32}H_{40}Cu_4S_2$
MW	205.58	742.97
cryst system	monoclinic	tetragonal
space group	$P2_1/c$ (No. 14)	$P4_2$ (No. 77)
a, Å	7.161 (1)	14.595 (2)
b, Å	6.636 (1)	
c, Å	11.039 (1)	7.513 (1)
β, deg	93.92 (1)	
V, Å^3	523.4 (1)	1600.4 (4)
Z	4	2
d(calcd), g/cm^3	2.609	1.542
F(000)	392	760
μ, cm^{-1}	119.6	27.8
cryst size, mm	0.16 × 0.37 × 0.30	0.70 × 0.27 × 0.20
temp, K	100	100
θ_{max}, deg	28.47	30.26
radiation, λ (Å)	Mo Kα (Zr-filtered), 0.71073	Mo Kα (Zr-filtered), 0.71073
scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$, deg	$0.65 + 0.35 \tan\theta$	$0.70 + 0.35 \tan\theta$
hor and vert aperture, mm	3.0, 5.0	3.0, 5.0
dist cryst to detector, mm	173	173
reference reflns	−2, 0, −4, 0, −2, −4, 2, −4, 0	−4, 2, 0, 103, 0, −1, 3
data set	h −9, 9; k −8, 8; l −14, 0	h 0, 20; k −20, 20; l 0, 10
total data	2756	7076
total unique data	1322	2558
observed data [$I > 2.5\sigma(I)$]	1225	2355
no. of refined params	54	214
weighting scheme	$w = [\sigma^2(F)]^{-1}$	$w = [\sigma^2(F) + 0.000336F^2]^{-1}$
final R, R_w, S	0.021, 0.023, 0.91	0.025, 0.030, 0.73
$(\Delta/\sigma)_{av}$ in final cycle	0.021	0.040
min and max resd densities, e/Å^3	−0.54, 0.70	−0.27, 0.44

[$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$]. To a stirred suspension of 3.13 g [$CuBr(SMe_2)$] (15.22 mmol) in 20 mL of diethyl ether maintained at −20 °C in a deep cooling bath was added by syringe a room-temperature solution of [$Li(C_6H_4Me\text{-}2)$]$_n$ in 30 mL of diethyl ether in less than 5 min. To prevent decomposition of the product, contact of the reaction mixture with the warmer upper parts of the Schlenk tube was carefully avoided. The yellow suspension obtained was stirred for 2 h, and then the solvent was removed under reduced pressure at −20 °C. The resultant powder was dissolved in 30 mL of dimethyl sulfide at room temperature and the remaining white residue of LiBr filtered off at this temperature. This solution is air-sensitive. Crystallization at −20 °C by diffusion of 100 mL of dry hexane into this dimethyl sulfide solution afforded pale-yellow crystals. The solvent was then decanted off, and the crystals were washed once with cold hexane and dried in vacuo. The yield was 1.15 g of [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$] (1.55 mmol, 41% based on [$CuBr(SMe_2)$]). As a solid, [$Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2$] ($C_{32}H_{40}Cu_4S_2$) is sensitive to air and is thermally unstable at room temperature. The crystals show visible decomposition above 50 °C (mp ca. 95 °C). Elemental analytical data (C, 48.45; H, 5.13; S, 7.54) when normalized to two sulfur atoms provide $C_{34}H_{43}Cu_5S_2$; this result is consistent with thermal loss of some organic moieties. The crystals can be stored under an atmosphere of nitrogen for at least 3 months without noticeable decomposition (^1H NMR spectroscopy), though for some redissolved samples the initial *o*-tolyl:DMS ratio of 2:1 had changed. ^1H NMR (benzene-d_6, 297 K): δ 8.1 (1 H, br s, *o*-H), 7.0 (3 H, m, *m*-, *p*-H), 2.6 (3 H, br s, CH_3), 1.3 (3 H, s, SCH_3). Temperature-dependent ^1H NMR spectra (toluene-d_8): 333 K, all signals of the aromatic ring are broad; room temperature, three sets of resonances for *o*-H, (*m* + *p*)-H, and *o*-Me; 307 K (*o*-H, d,

---

[5] Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1427.

[6] San Filippo, J.; Zyontz, L. E.; Potenza, J. *Inorg. Chem.* **1975**, *14*, 1667.

[7] Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: London, 1987; Vol. 5, p 533.

[8] van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *84*, 129.

[9] van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 2, Chapter 14, p 709.

[10] van Koten, G.; Jastrzebski, J. T. B. H. *Tetrahedron* **1989**, *45*, 569.

$J = 7$ Hz). The shift of the methyl group of the dimethyl sulfide group is temperature-dependent, and the shifts measured range from 0.7 ppm (−70 °C) to 1.5 ppm (+60 °C). After this series of experiments, the spectrum recorded at room temperature was the same as the one first measured.

Crystal Structure Determination of [CuBr(SMe$_2$)]. Collection and Treatment of X-ray Diffraction Data. Crystal data and numerical details of the structure determination are given in Table I. Crystals were obtained by diffusion of hexane into a solution of [CuBr(SMe$_2$)] in dimethyl sulfide. A platelike colorless crystal was collected and mounted on a glass fiber and transferred to an Enraf-Nonius CAD4F diffractometer for data collection at 100 K. Unit cell parameters were determined from a least-squares fit of the SET4 setting angles of 25 reflections with $12.6 < \theta < 19.4°$ and were checked for the presence of higher lattice symmetry.[11] There was negligible decay (<0.5%) during the 36 h of X-ray exposure time. Data were corrected for Lp and for absorption (ABSORB,[12] correction range 5.27–13.60) and merged into an unique data set ($R_{int} = 7\%$). Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the three reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.012I)^2$.[13]

Structure Determination and Refinement. The structure was solved with automated Patterson interpretation followed by peak optimization (SHELXS86).[14] Refinement on F was carried out by full-matrix least-squares techniques (SHELX76).[15] Hydrogen atoms were introduced at calculated positions [C–H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with one common isotropic thermal parameter [$U = 0.018$ (4) Å^2]. Empirical extinction correction [$F^{corr} = F(1 - xF^2/\sin(\theta)$, with $x = 5.1 (2) \times 10^{-7}$] was applied. Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.021$.

Crystal Structure Determination of [Cu$_4$(C$_6$H$_4$Me-2)$_4$(SMe$_2$)$_2$]. Collection and Treatment of X-ray Diffraction Data. Crystal data and numerical details of the structure determination are given in Table I. A plate-shaped crystal was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4F diffractometer for data collection at 100 K. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $12.3 < \theta < 19.3°$ and were checked for the presence of higher lattice symmetry.[11] Data were corrected for Lp and for a small linear decay (1.5%) of the intensities during the 112 h of X-ray exposure time but not for absorption. Data were merged into an unique data set ($R_{int} = 4.3\%$).

Structure Determination and Refinement. The structure was solved with direct methods (SHELXS86)[14] and a series of subsequent difference Fourier syntheses. A disorder model was used to describe the (3:1) positional disorder of the C(1)–C(7) tolyl group. Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions [C–H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were refined with two separate common isotropic thermal parameters [$U = 0.061$ (5) Å^2 for methyl H atoms; $U = 0.052$ (6) Å^2 for other H atoms]. Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.025$. The absolute structure was checked by refinement with $-\Delta f''$ anomalous scattering factors resulting in $R = 0.029$; $R_w = 0.035$. For both structure determinations, neutral atom scattering factors[16] were corrected for anomalous dispersion.[17] All calculations were performed with SHELX76[15] and the EUCLID package[18] (geometrical calculations and illustrations) on a MicroVAX cluster.

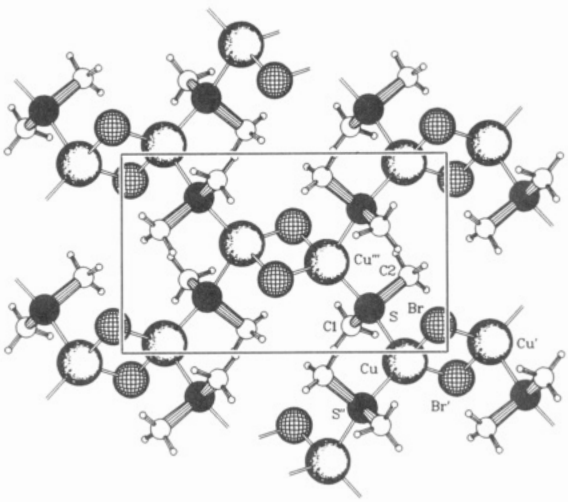

Figure 1. Structure and labeling scheme of [CuBr(SMe$_2$)].

Table II. Bond Distances (Å) and Bond Angles (deg) of [CuBr(SMe$_2$)]^a

Br–Cu	2.5010 (6)	Cu–S″	2.2895 (8)
Br–Cu′	2.4441 (6)	S–Cu(1)	1.809 (3)
Cu–Cu′	2.9512 (6)	S–C(2)	1.800 (3)
Cu–S	2.3541 (8)		
Cu–Br–Cu′	73.27 (2)	Cu–S–Cu‴	131.79 (3)
Br–Cu–Br′	106.73 (2)	Cu–S–C(1)	107.51 (9)
Br–Cu–S	100.60 (2)	Cu–S–C(2)	102.1 (1)
Br–Cu–S″	108.80 (2)	Cu‴–S–C(1)	109.8 (1)
Br′–Cu–S	104.75 (2)	Cu‴–S–C(2)	100.7 (1)
Cu′–Cu–S	111.52 (2)	C(1)–S–C(2)	99.6 (1)
S–Cu–S″	110.48 (3)		

^{a} Symmetry code: ′, $-x, -y, -z$; ″, $-x, y - {}^1/_2, {}^1/_2 - z$; ‴, $-x, {}^1/_2 + y, {}^1/_2 - z$.

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters of [CuBr(SMe$_2$)] and Their Esd's in Parentheses

atom	x	y	z	U(eq),^{a} Å^2
Br	0.247 40 (4)	0.133 04 (4)	0.027 53 (2)	0.0098 (1)
Cu	−0.004 39 (5)	−0.047 50 (5)	0.130 36 (3)	0.0106 (1)
S	−0.131 47 (9)	0.219 91 (9)	0.238 18 (6)	0.0082 (2)
C(1)	−0.348 4 (4)	0.131 9 (4)	0.294 4 (3)	0.0127 (8)
C(2)	−0.223 6 (4)	0.381 6 (4)	0.117 6 (3)	0.0138 (8)

^{a} U(eq) = $^1/_3$ of the trace of the orthogonalized **U** matrix.

Results and Discussion

Structure of [CuBr(SMe$_2$)]. The copper bromide–dimethyl sulfide adduct [CuBr(SMe$_2$)], whose synthesis has been reported earlier,[1] was crystallized by slow distillation of hexane into a saturated solution of [CuBr(SMe$_2$)] in DMS. An X-ray single-crystal diffraction study has been carried out and the polymeric structure refined to $R = 0.021$ for 1225 reflections. The unit cell contents and the molecular geometry of the single repeating [CuBr(SMe$_2$)] entity with its labeling scheme and structural connectivities are shown in Figure 1. The relevant distances and angles are presented in Table II and the positional parameters are to be found in Table III. The compound forms an infinite two-dimensional layer structure with a network that is based on Cu$_2$Br$_2$ parallelepipeds comprising two copper atoms bridged by two bromine

---

(11) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(12) Spek, A. L. ABSORB, program for absorption correction; University of Utrecht: Utrecht, The Netherlands, 1983; ECM Abstracts Book, p 283.

(13) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245.

(14) Sheldrick, G. M. SHELXS86, program for crystal structure determination; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

(15) Sheldrick, G. M. SHELX76, program for crystal structure determination; University of Cambridge: Cambridge, England, 1976.

(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(17) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(18) Spek, A. L. The Euclid package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528.

Table IV. Comparison of Bond Distances and Bond Angles in Cu_2Br_2 Cores

compd	Cu···Cu, Å	Cu–Br–Cu, deg	Cu–Br, Å
$[CuBr(SMe_2)]$[a]	2.9512 (6)	73.27 (2)	2.5010 (6), 2.4441 (6)
$(NEt_4)_2[Cu_2Br_4]$[b]	2.937 (3)	73.7 (1)	2.454 (2), 2.441 (2)
$[Cu_2Br_2(PPh_3)_3]$[c]	2.992 (2)	71.88 (5), 71.66 (5)	2.370 (2)–2.610 (2)

[a] This work. [b] Reference 19. [c] Reference 20.

Table V. Final Coordinates and Equivalent Isotropic Thermal Parameters of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ and Their Esd's in Parentheses

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Cu(1)	0.09218 (2)	0.39812 (2)	0.2343	0.0202 (1)
Cu(2)	0.06965 (2)	0.56021 (2)	0.27966 (8)	0.0230 (1)
S	0.16089 (5)	0.26522 (5)	0.1315 (1)	0.0261 (2)
#C(1)[b]	0.1881 (3)	0.5000 (3)	0.2056 (6)	0.026 (1)
#C(2)	0.2552 (5)	0.5001 (4)	0.346 (1)	0.035 (2)
#C(3)	0.3457 (3)	0.5257 (3)	0.311 (1)	0.047 (2)
#C(4)	0.3716 (3)	0.5517 (4)	0.140 (1)	0.058 (2)
#C(5)	0.3087 (4)	0.5512 (4)	0.001 (1)	0.037 (2)
#C(6)	0.2169 (3)	0.5274 (3)	0.0340 (7)	0.029 (1)
#C(7)	0.1499 (6)	0.5273 (5)	−0.117 (1)	0.038 (2)
C(8)	0.0053 (2)	0.6601 (2)	0.4031 (4)	0.0221 (7)
C(9)	−0.0279 (2)	0.6388 (2)	0.5759 (4)	0.0281 (8)
C(10)	−0.0329 (2)	0.7026 (3)	0.7111 (5)	0.036 (1)
C(11)	−0.0041 (2)	0.7917 (3)	0.6790 (5)	0.038 (1)
C(12)	0.0293 (2)	0.8149 (2)	0.5140 (5)	0.034 (1)
C(13)	0.0355 (2)	0.7509 (2)	0.3758 (5)	0.0256 (8)
C(14)	0.0758 (3)	0.7788 (3)	0.1998 (5)	0.036 (1)
C(15)	0.2117 (2)	0.2262 (2)	0.3364 (5)	0.035 (1)
C(16)	0.2626 (3)	0.2904 (3)	0.0064 (6)	0.037 (1)
	Minor Disorder Atoms [sof = 0.251 (6)]			
C(100)	0.1595 (8)	0.5024 (8)	0.112 (2)	0.019 (2)
C(200)	0.144 (2)	0.518 (2)	−0.071 (3)	0.030 (5)
C(300)	0.206 (1)	0.543 (1)	−0.194 (2)	0.041 (4)
C(400)	0.295 (1)	0.550 (1)	−0.134 (2)	0.039 (3)
C(500)	0.319 (1)	0.538 (1)	0.054 (3)	0.029 (4)
C(600)	0.253 (1)	0.515 (1)	0.164 (2)	0.031 (3)
C(700)	0.280 (1)	0.499 (2)	0.335 (3)	0.033 (6)

[a] *U*(eq) = $^1/_3$ of the trace of the orthogonalized **U** matrix. [b] # indicates major disorder atom [sof = 0.749 (6)].

atoms. These units are linked together by dimethyl sulfide groups in such a way that each copper atom is connected through two dimethyl sulfide groups to two further separate Cu_2Br_2 units. The resulting network structure is clearly seen in Figure 1. The geometry of the Cu_2Br_2 unit of $[CuBr(SMe_2)]_n$, with the copper atoms being coordinated in a distorted tetrahedral fashion, is comparable to those of the dinuclear compounds $(NEt_4)_2[Cu_2Br_4]$[19] and $[Cu_2Br_2(PPh_3)_3]$;[20] see Table IV. In $[CuBr(SMe_2)]_n$, the sulfur atoms of dimethyl sulfide bridging between the Cu_2Br_2 units have a severely distorted tetrahedral coordination sphere with a Cu–S–Cu angle of 131.79 (3)° (cf. 118.6° in $[Cu_4I_4(SEt_2)_3]$.[6]

The adduct $[CuBr(SMe_2)]_n$ is one of the few copper compounds with a two-dimensional layered structure,[7] and it is probably this polymeric nature that provides the insolubility of this compound in most common solvents. The reasonable solubility of $[CuBr(SMe_2)]_n$ in DMS is likely to be the result of equilibria in which the polynuclear structure breaks down to lower order clusters of the type $[CuBr(SMe_2)_{1+x}]_y$.

Preparation and Structure of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$. Starting from $[CuBr(SMe_2)]_n$ and *o*-tolyllithium, we have prepared the *o*-tolylcopper–dimethyl sulfide adduct $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ (eq 1). Careful

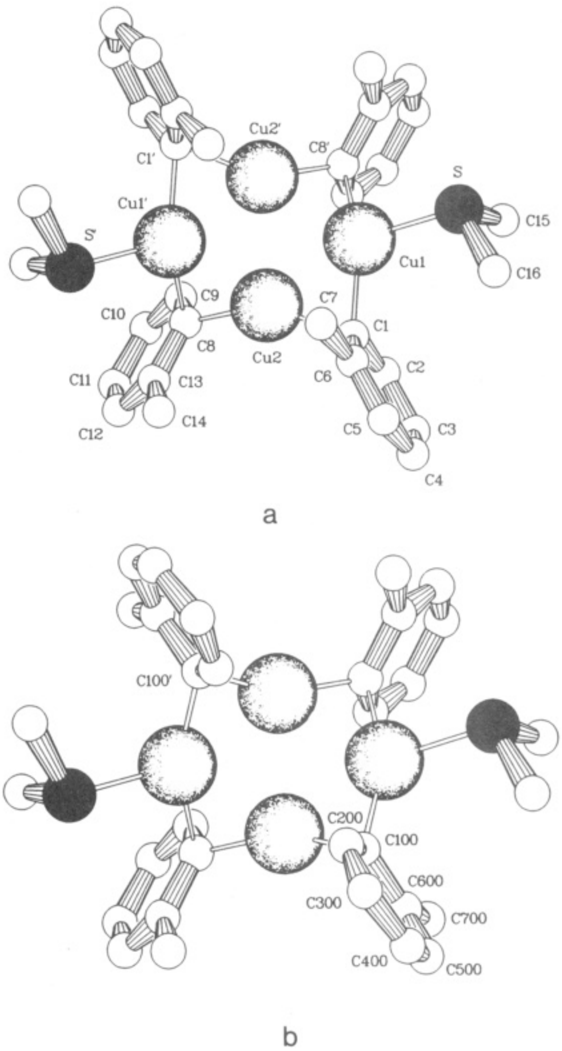

Figure 2. Plot of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ with adopted labeling scheme (hydrogen atoms omitted for clarity); (a) α conformer (74.9(6)%), (b) β conformer (25.1(6)%).

$$(4/n)[CuBr(SMe_2)]_n + 4Li(C_6H_4Me\text{-}2) \rightarrow [Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2] + 4LiBr + 2SMe_2 \quad (1)$$

control of the reaction temperature as well as the reaction time is crucial for successful preparation of the pure *o*-tolylcopper compound in high yield. Temperatures higher than −20 °C cause rapid decomposition with formation of a copper mirror. Prolonged stirring of the reaction mixture also leads to decomposition, whereas shorter reaction times result in difficulties with the separation of the product from unreacted starting material. The synthesis of *o*-tolylcopper failed when excess DMS was present, and this led us to use diethyl ether for the successful preparation of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$. However, the use of DMS as solvent for the purification and crystallization of the crude product appeared to be indispensable. Once isolated, the pale-yellow crystalline compound undergoes slow thermal decomposition at room temperature that eventually leads to formation of a copper mirror. Elemental analytical data (see Experimental Section) are consistent with partial loss of the organic groups. Solid $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ does not react with dry air, but traces of moisture do lead to rapid decomposition.

An X-ray single-crystal diffraction study of this 2:1 *o*-tolylcopper–DMS adduct has been carried out and the

---

(19) Asplund, M.; Jagner, S. *Acta Chim. Scand.* **1984**, *A38*, 135.

(20) Negita, H.; Hiura, M.; Kushi, Y.; Kuramoto, M.; Okuda, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1247.

Table VI. Selected Bond Distances (Å) and Angles (deg) of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$[a]

Cu(1)–Cu(2)	2.4126 (5)	Cu(2)–C$^{\alpha}$(1)	2.018 (4)
Cu(1)–Cu(2)′	2.4626 (5)	Cu(2)–C$^{\beta}$(100)	2.01 (1)
Cu(2)–Cu(2)′	2.6874 (6)	Cu(2)–C(8)	1.967 (3)
Cu(1)–Cu(1)′	4.0105 (7)	Cu(1)–S	2.3160 (9)
Cu(1)–C(8)′	2.087 (3)	S–C(15)	1.801 (4)
Cu(1)–C$^{\alpha}$(1)	2.054 (4)	S–C(16)	1.795 (4)
Cu(1)–C$^{\beta}$(100)	2.03 (1)		
Cu(2)–Cu(1)–Cu(2)′	66.89 (1)	Cu(2)–Cu(1)–C$^{\alpha}$(1)	53.0 (1)
Cu(1)–Cu(2)′–Cu(2)	55.66 (1)	Cu(1)–Cu(2)–C$^{\alpha}$(1)	54.3 (1)
Cu(1)–Cu(2)–Cu(2)′	57.44 (1)	Cu(1)–C$^{\alpha}$(1)–Cu(2)	72.7 (2)
Cu(1)–Cu(2)–Cu(1)′	110.69 (2)	Cu(2)–Cu(1)–C$^{\beta}$(100)	52.8 (3)
S–Cu(1)–C$^{\beta}$(100)	105.5 (3)	Cu(1)–Cu(2)–C$^{\beta}$(100)	53.8 (3)
S–Cu(1)–C$^{\alpha}$(1)	106.0 (1)	Cu(1)–C$^{\beta}$(100)–Cu(2)	73.4 (4)
S–Cu(1)–C(8)′	99.02 (8)	C(8)–Cu(2)–Cu(1)′	54.84 (9)
C$^{\alpha}$(1)–Cu(1)–C(8)′	145.4 (2)	Cu(2)–Cu(1)′–C(8)	50.40 (8)
C$^{\beta}$(100)–Cu(1)–C(8)′	155.5 (3)	Cu(2)–C(8)–Cu(1)′	74.8 (1)
C(8)–Cu(2)–C$^{\beta}$(100)	157.0 (3)	Cu(1)–S–C(15)	99.1 (1)
C$^{\alpha}$(1)–Cu(2)–C(8)	149.6 (2)	Cu(1)–S–C(16)	111.2 (1)
Cu(2)–Cu(1)–S	158.02 (2)	C(15)–S–C(16)	99.9 (2)
S–Cu(1)–Cu(2)′	131.93 (2)		

[a] Symmetry code: ′, $-x$, $1 - y$, z.

structure refined to $R = 0.025$ for 2355 reflections. The crystal structure is based on discrete tetranuclear copper clusters of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$, and the molecular structure together with the labeling scheme is depicted in Figure 2. The final atomic coordinates are given in Table V, and selected bonding angles and distances are collected in Table VI. Each cluster has a virtually planar, "flattened butterfly", Cu_4 core with adjacent copper atoms being bridge-bonded by a C_{ipso} atom of one *o*-tolyl group. Two nonadjacent copper atoms are each further bonded to the sulfur atom of a coordinating dimethyl sulfide. The investigated crystal of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ has some *o*-tolyl group disorder, and the cluster in fact exists as two different geometric conformers (α and β) that differ only in the exact positioning and orientation of one pair of *o*-tolyl ligands. In the major α conformer (75%, Figure 2a), the methyl groups of the four *o*-tolyl ligands are all to one side of the Cu_4 plane. However, in the β conformer (Figure 2b), the pairs of opposing *o*-tolyl groups have their methyl groups on opposite sides of the Cu_4 core. The bonding description of the cluster for both conformers is the same, and both have a 2-fold rotation axis perpendicular to the copper core.

In the Cu_4 cluster one pair of opposite copper atoms [Cu(2), Cu(2)′] is digonally bonded to two *o*-tolyl ligands (∠C(8)–Cu(2)–C$^{\alpha}$(1) = 149.6 (2)°, ∠C(8)–Cu(2)–C$^{\beta}$(100) = 157.0 (3)°). Each of the other "wing tip" pairs of copper atoms [Cu(1), Cu(1)′] is pseudotrigonally coordinated (sum of the angles is 350.5° for α and 360.0° for β) by two *o*-tolyl ligands and a dimethyl sulfide molecule such that the Cu(I) coordination sphere is best described as T-shaped (∠C$^{\alpha}$(1)–Cu(1)–C(8)′ = 145.4 (2)°, ∠C$^{\beta}$(100)–Cu(1)–C(8)′ = 155.5 (3)°). The distance of 4.0105 (7) Å between the copper atoms on the wing tips is much larger than that of 2.6874 (6) Å between those of the body. The dihedral angle between the wing planes (defined by the triangles Cu(2)Cu(2)′Cu(1)′ and Cu(2)Cu(2)′Cu(1)) is only 160.7 (3)°. In both the α and β conformers, the C_{ipso} atoms of the bridging *o*-tolyl ligands are positioned alternately above and below the Cu_4 core. As anticipated,[9] the atoms of each Cu_2C_{ipso} triangular unit and the corresponding C_{para} atom lie in one plane with the aryl ring plane orientated approximately perpendicular to this plane (for example, these interplane angles are 83.3 (2), 86.5 (6), and 80.8 (1)° for the C$^{\beta}$(1), C$^{\alpha}$(1), and C(8) rings, respectively).

The coordination sphere of the sulfur atoms is distorted tetrahedral, and the geometric features can be interpreted in terms of a dimethyl sulfide molecule coordinating with one of the two sulfur electron lone pairs. The values of the angles and distances of the dimethyl sulfide molecule of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ are similar to those of the dimethyl sulfide bonded to gold(I) in $[AuBr(SMe_2)]$.[21]

The overall molecular structure of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ closely resembles that previously reported for $[Cu_4(C_6H_2Me_3\text{-}2,4,6)_4(SC_4H_8)_2]$ (SC_4H_8 = tetrahydrothiophene).[22] However, compared to $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ and particularly its DMS-free analogue $[Cu_4(C_6H_4Me\text{-}2)_4]$, the mesityl copper species $[Cu_4(C_6H_2Me_3\text{-}2,4,6)_4(SC_4H_8)_2]$ and $[Cu_5(C_6H_2Me_3\text{-}2,4,6)_5]$ can be synthesized relatively easily in high yields and, moreover, the latter both have a much higher thermal stability than pure *o*-tolylcopper. These observed differences in the stability and in the ease of synthesis of closely related organocopper compounds can be rationalized when the stabilizing effects of additional coordination of Lewis bases and the presence of bulky organo groups are taken into account.[9]

In the present case of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$, we believe that it is the presence of the *o*-tolyl substituent and of DMS as a Lewis base that together provide the key to the higher stability of this adduct, compared to that of uncomplexed *o*-tolylcopper. The fact that *o*-tolylcopper species are in general more fragile than the mesitylcopper compounds is consistent with the greater stabilizing effect that two *o*-methyl groups have over one on the stability of (aryl)C_{ipso}–Cu bonding.[8,10,23,24]

Arylcopper compounds in which bulky ortho substituents on the aromatic ring afford stabilization include the monomeric species $[Cu(C_6H_2Ph_3\text{-}2,4,6)]$[25] and the tetrameric species $[Cu(C_6H_2Pr^i_3\text{-}2,4,6)]_4$[26] and $[Cu(C_6H_2Me_3\text{-}2,4,6)]_4$[27]; n.b., the type of ortho group (Ph, Pr^i, or Me) also affects the nature of the C_{ipso}–Cu bonding.[10] Stabilization by coordination of a Lewis base is represented by $[Cu_4(C_6H_2Me_3\text{-}2,4,6)_4(SC_4H_8)_2]$.[22] The combination of both effects is found in organocopper compounds with chelating aryl ligands; a good example from our laboratory is the tetrameric structure of (8-(dimethylamino)-1-naphthyl)copper(I) in which each C_{ipso} is three-center two-electron bonded to two copper atoms while the dimethylamino group coordinates to one of these copper centers.[28]

In previous papers on the stereochemistry of arylcopper compounds with ortho chelating groups, e.g., $[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4]$,[10] we have described the three-center two-electron C_{ipso}–Cu_2 bonding of the ortho-substituted aryl group. Therein possible rotation of the aryl ring about the C_{ipso}–C(4) axis was discussed, and we suggested that the more stable rotamers are those with their aryl ring planes perpendicular to the Cu···Cu vector.[10,29,30] So far only indirect proof for this idea has been obtained from various ^{1}H, ^{13}C, ^{7}Li, and ^{109}Ag NMR studies of [Cu$_4$-

---

[21] Nifontova, G. A.; Krasochka, O. N.; Lavrent'ev, I. P.; Makitova, D. D.; Atovmyan, L. O.; Khidekel, M. L. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1988**, *37*, 2386.

[22] Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

[23] van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Org. Chem.* **1977**, *42*, 2047.

[24] Wehman, E.; van Koten, G.; Erkamp, C. J. M.; Knotter, D. M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Organometallics* **1989**, *8*, 94.

[25] Lingnau, R.; Strähle, J. *Angew. Chem.* **1988**, *100*, 409.

[26] Nobel, D.; van Koten, G.; Spek, A. L. *Angew. Chem.* **1989**, *101*, 211.

[27] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1157.

[28] Wehman, E.; van Koten, G.; Knotter, M.; Spelten, H.; Heijdenrijk, D.; Mak, A. N. S.; Stam, C. H. *J. Organomet. Chem.* **1987**, *325*, 293.

[29] van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 6593.

[30] van Koten, G.; Jastrzebski, J. T. B. H.; Stam, C. H., Brevard, C. In *Biological and Inorganic Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1985; p 267.

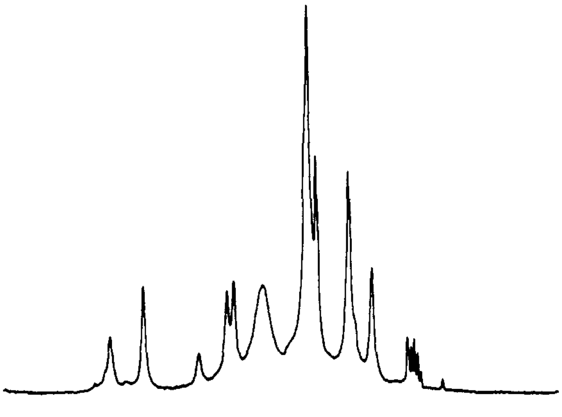

Figure 3. ^{1}H NMR spectrum (200 MHz, toluene-d_8, −30 °C) of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$; *o*-methyl region.

$(C_6H_4CH_2NMe_2\text{-}2)_4]$, diastereoisomeric $[Cu_4(C_6H_4CHMeNMe_2\text{-}2)_4]$, and the cuprates and argentates $[Li_2M_2(C_6H_4CH_2NMe_2\text{-}2)_4]$ (M = Cu or Ag).[10] The presence of the two conformers, α and β, in the crystal structure of tetranuclear $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ now provides direct support for our previous suggestion.

Structure in Solution. The ^{1}H NMR (200 MHz, toluene-d_8) spectrum of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ is temperature-dependent. When recorded at +60 °C, the simple pattern of signals it exhibits is consistent with all the *o*-tolyl ligands being equivalent. The spectrum consists of sharp singlets for the dimethyl sulfide and *o*-methyl groups, a signal at 8.0 ppm which is characteristic for the ortho proton of the tolyl ligand and a multiplet at ca. 7.0 ppm for the other aromatic protons. At room temperature, the spectrum of this compound contains broad signals for all the *o*-tolyl group protons though the singlet for the dimethyl sulfide remains sharp. At −30 °C, the slow exchange limit appears to be reached and the complex spectrum shows well-defined resonances for at least eight different types of *o*-tolyl groups; the pattern in the *o*-methyl group region is shown in Figure 3. A ^{13}C NMR spectrum at −30 °C also showed the presence of many different *o*-tolyl groupings. The complexity of the low-temperature spectra can be easily understood when it is accepted that in the slow exchange limit each bridging C_{ipso} atom is tetrahedrally coordinated (see the solid-state structures of conformers α and β). Each C_{ipso} atom is thus rendered stereogenic because it not only bridges two copper atoms with different coordination geometries (two- and three-coordinate, respectively, as a result of DMS coordination) but also binds to two different ortho-carbon atoms. Following the Cahn–Ingold–Prelog sequence rules, the configuration of each of the four C_{ipso} centers in the various conformers can be designated (*S*) or (*R*), and accordingly, there are many (*R*/*S*,*R*/*S*,*R*/*S*,*R*/*S*) diastereoisomers possible; for example, the α and β conformers are the (*S*,*R*,*S*,*R*) and (*R*,*R*,*R*,*R*) diastereoisomers, respectively.

We believe that the numerous signals of the low-temperature NMR spectra of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ correspond to the presence and detection of many, if not all, of the possible diastereoisomeric conformers with their differing orientation patterns of the *o*-tolyl ligands. Fluxional processes that can interconvert the relative orientations of *o*-tolyl groups are then responsible for the temperature dependence of the NMR spectra and the equivalence of all *o*-tolyl groups above room temperature. The interconversion process is probably based on rotation of the *o*-tolyl ligands about the C_{ipso}–C(4) axis at the copper core together with (concomitant) inversion of the butterfly Cu_4 structure. It is also possible for inversion of configuration of the C_{ipso} centers to occur by rotation of the aryl ring around the C_{ipso}–C(4) axis in combination with dissociation of the Cu–DMS bonds and subsequent recoordination of the DMS at the other copper atom pair. We have evidence for a ready exchange between coordinated and uncoordinated DMS from the temperature dependence of the DMS ^{1}H NMR signal and further NMR experiments with added DMS. It would appear that the various diastereoisomeric conformers of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ do not differ significantly in their thermodynamic stabilities but it would require elaborate NMR studies to fully interpret the low-temperature NMR spectra in terms of assignments and relative abundances.

The dimethyl sulfide free pure *o*-tolylcopper complex $[Cu_4(C_6H_4Me\text{-}2)_4]$ was reported to have temperature-dependent ^{1}H NMR spectra (90 MHz, $CDCl_3$);[31] these data can likewise be interpreted in terms of the existence of different conformers, which in this case interconvert rapidly on the NMR time scale at 0 °C.

Conclusion

The current results show the successful application of a DMS–Cu(I) adduct $[CuBr(SMe_2)]$ to the synthesis of a pure organocopper species. This approach clearly has much potential for the synthesis and isolation of labile organocopper compounds and organocopper reagents whose use had been previously restricted by ill-defined in situ preparations.

One fascinating aspect of the crystal structure of $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ is the presence of two conformers that differ with respect to the exact positioning and the mutual orientation of the *o*-methyl groups of the four, three-center, two-electron bridge-bonded *o*-tolyl groups. This is the first unambiguous experimental proof for such conformers whose existence had been earlier anticipated on the basis of solution ^{1}H NMR data for arylcopper and arylcuprate species.

Acknowledgment. The X-ray data were collected by A. J. M. Duisenberg. This work was supported in part (A.L.S., W.J.J.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). B.L. thanks the E.E.C. for a generous grant (No. ST2*-0107).

Supplementary Material Available: Tables of anisotropic thermal parameters, H atom positions, and all bond distances and angles and ORTEP plots for $[CuBr(SMe_2)]$ and $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$ (9 pages); a list of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

---

(31) Hofstee, H. K.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* 1978, *144*, 255.