Organometallics 1992, *11*, 4083-4090

Novel Trinuclear and Hexanuclear Heteroorganocopper Compounds with Phosphine Ligands, Bridging Alkynyls, and Intramolecularly Coordinating Bridging Arenethiolates. X-ray Structures of $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (R = H, Me)

D. Martin Knotter,[†] Anthony L. Spek,[‡] David M. Grove,[†] and Gerard van Koten*,[†]

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

Received March 19, 1992

(Arenethiolato)alkynylcopper(I) complexes $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (R = H, Me) with an intramolecularly coordinating ligand have been prepared from the reaction of $[CuSC_6H_4(CH(R)NMe_2)\text{-}2]_3$ with either $CuC{\equiv}C\text{-}t\text{-}Bu$ or $LiC{\equiv}C\text{-}t\text{-}Bu$. Crystals of $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (**3**) are monoclinic with $a = 11.213$ (1) Å, $b = 18.360$ (2) Å, $c = 13.118$ (1) Å, $\beta = 103.72$ (1)°, space group $P2_1/c$, $Z = 2$, and $R = 0.061$ for 1956 reflections with $I \geq 3\sigma(I)$ and 305 variables. Crystals of $[Cu_3\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (**4**) are monoclinic with $a = 11.600$ (2) Å, $b = 17.071$ (3) Å, $c = 15.513$ (3) Å, $\beta = 101.53$ (1)°, space group $P2_1$, $Z = 2$, and $R = 0.056$ for 5573 reflections with $I \geq 2.5\sigma(I)$ and 647 variables. Each structure contains two $Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)$ units that have Cu_3S_2C six-membered rings in a boatlike conformation with alternating copper and sulfur or carbon atoms. Through side-on coordination of the bridging alkynyl group of one unit to a coordinatively unsaturated copper atom of a second unit a hexanuclear structure is formed. This is the first example of a symmetrical (μ_3-C$^\alpha$, μ_1-C$^\beta$)-η^2 bridging alkynyl group. In the crystal structures the orientation of the ligands affords two conformers of the $Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)$ units; in solution ^{1}H NMR provides evidence for three conformations which are in equilibrium with a low free activation energy barrier. Furthermore, there is an equilibrium between the hexanuclear structure and two trinuclear units. Hexanuclear **3** and **4** react with phosphine ligands (L) to form the trinuclear heteroorganocopper species $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)(L)]$. Our results show that in addition to anionic species neutral $Cu_3(SAr)_2(C{\equiv}C\text{-}t\text{-}Bu)$ species that have a reactive site with specific Lewis acidic properties can also be present in cuprate reagent mixtures.

Introduction

The use of copper compounds, with both organic and inorganic ligands, has been investigated extensively in organic synthetic chemistry,[1] and cuprates are the postulated reactive species in many copper-mediated organic reactions.[2] The addition of an excess of an organometallic reagent to a copper salt initially leads to the formation of a cuprate.[3] However, this reaction does not provide one discrete species, and there is little known about the structures of the species present in these solutions.[4] Moreover, the nature of the reactive species in reactions with organic substrates is in most cases still undefined.

The equilibrium between the different species in a cuprate solution can be influenced by the variation of the ligand system bonded to copper. With Cu(I)-stabilizing ligands, like thiolates, we should expect preferential formation and stabilization of some species which may then be isolable. We have selected a thiophenolate with a potential intramolecularly coordinating amine group to provide extra stabilizing properties. Using this monoanionic, bidentate N,S-ligand enabled us to prepare the pure copper arenethiolates $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (**1**) and $[CuSC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2]_3$ (**2**).[5a,b] They are trimeric copper compounds with bridging sulfur atoms and intramolecularly coordinating amine groups.

Most organocopper compounds have a low solubility in organic solvents, are thermally unstable, and are also very sensitive toward moisture and air. However, (3,3-dimethyl-1-butynyl)copper is a stable compound which is soluble in a wide scale of solvents. Thus, when copper arenethiolates are mixed with (3,3-dimethyl-1-butynyl)lithium stable mixed organic organocuprate or -copper compounds should result. Here, we wish to report our findings on products of this reaction.[5c]

Experimental Section

Syntheses were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were carefully dried and distilled prior to use. Commercial *n*-BuLi (1.56 M in hexane) and 3,3-dimethyl-1-butyne were used. $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (**1**) and $[CuSC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2]_3$ (**2**) were prepared according to literature methods.[5]

^{1}H NMR spectra were recorded on a Bruker AC-200P spectrometer, and IR spectra were measured on a Perkin-Elmer 283

---

* To whom correspondence should be addressed.

[†] Debye Research Institute.

[‡] Laboratory of Crystal and Structural Chemistry.

(1) (a) Lipshutz, B. H. *Synthesis* **1987**, *325*. (b) Posner, G. H. *An Introduction to Synthesis using Organocopper Reagents*; Wiley Interscience: New York, 1980. (c) Normant, J. F. *Synthesis* **1972**, *63*.

(2) (a) Whitesides, G. M.; Fischer, W. F., Jr.; San Fillipo, J., Jr.; Baske, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. (b) House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2770.

(3) Gilman, H.; Strahley, J. M. *Recl. Trav. Chim. Pays-Bas* **1936**, *55*, 821.

(4) (a) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197. (b) Lipshutz, B. H.; Parker, D. A.; Nguyu, S. L.; McCarthy, K. E.; Barton, J. C.; Whitney, S. E.; Kotsaki, H. *Tetrahedron* **1986**, *42*, 2873. (c) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668. (d) Ashby, E. C.; Goel, A. B. *J. Org. Chem.* **1983**, *48*, 2125.

(5) (a) Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 3309. (b) Knotter, D. M.; van Koten, G.; van Maanen, H. L.; Grove, D. M.; Spek, A. L. *Angew Chem.* **1989**, *101*, 351; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 341. (c) For a preliminary account on the preparation of **3** and full crystallographic data, see: Knotter, D. M.; Spek, A. L.; Van Koten, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1738.

0276-7333/92/2311-4083$03.00/0

IR spectrophotometer. Cryoscopic molecular weight determinations were carried out in benzene under dry oxygen-free nitrogen. Ebulliometric molecular weight determinations were carried out in CH_2Cl_2 under dry oxygen-free nitrogen using pure, boiling CH_2Cl_2 as constant reference. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Synthesis of $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (3). To a solution of 3,3-dimethyl-1-butyne (0.55 g, 6.7 mmol) in 20 mL of diethyl ether was added BuLi in hexane (4 mL, 6.7 mmol). The resulting solution was added to a suspension of CuBr (0.96 g, 6.7 mmol) and $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (1) (3.1 g, 4.5 mmol) in 20 mL of diethyl ether. After the reaction mixture was stirred for 1 h, the yellow suspension was filtered off. The solid was washed twice with 10-mL portions of diethyl ether whereafter it was dissolved in dichloromethane. This solution was concentrated and cooled to −20 °C. The crystals formed were filtered off and washed with 10 mL of diethyl ether. This yielded 3.55 g (88%) of yellow crystalline 3; mp >180 °C dec. Anal. Calcd for $C_{24}H_{33}Cu_3N_2S_2$: C, 47.70; H, 5.50; N, 4.64; S, 10.61. Found: C, 47.40; H, 5.32; N, 4.63; S, 10.70. ^1H NMR data are presented in Table IV.

Reaction of (3,3-Dimethyl-1-butynyl)lithium with 1. To a solution of (3,3-dimethyl-1-butynyl)lithium (1.03 g, 11.7 mmol) in 50 mL of tetrahydrofuran (THF) at 0 °C was added 1 (2.67 g, 11.7 mmol). After the reaction mixture was stirred for 1 h, the yellow suspension was filtered off and the solid was washed twice with 10-mL portions of THF. The volatiles were removed in vacuo, and 1.56 g (44%) of pure 3 was obtained with properties identical to those given above; a flame test indicated the absence of lithium salts.

Synthesis of $[Cu_3\{SC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (4). 3,3-Dimethyl-1-butyne (0.69 g, 8.4 mmol) in 10 mL of diethyl ether was reacted with BuLi in hexane (5.4 mL, 8.4 mmol). The volatiles were removed in vacuo, and the remaining dry solid was dissolved in 10 mL of benzene. This solution was added to $[CuSC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2]_3$ (2) (3.88 g, 5.3 mmol) and $[CuBr\{P(OMe)_3\}]$ (2.12 g, 7.9 mmol) in 50 mL of benzene. The color of the solution immediately turned bright yellow, and finely divided LiBr precipitated. After filtration, the filtrate was concentrated by distillation to 15 mL and 50 mL of hexane was added. The solution was warmed to 60 °C until all solids were dissolved and then cooled to room temperature. Compound 4 crystallized out as yellow triboluminescent crystals of its benzene solvate: yield 4.9 g of 4·benzene (72%); mp 182–186 °C (slow dec); $d = 1.433$ g cm^{-3} (by flotation in a mixture of $CHCl_3$ and CH_2Cl_2). Anal. Calcd for $C_{52}H_{74}Cu_6N_4S_4{\cdot}C_6H_6$: C, 51.88; H, 6.00; N, 4.19; O, 0.0. Found: C, 51.44; H, 6.32; N, 4.15; O, <0.2. ^1H NMR data are presented in Table IV.

Formation of $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)(PPh_3)]$ (5) by Ebulliometric Titration of 4 with PPh_3. To 4 (0.5889 g) in 12 mL of CH_2Cl_2 were added accurately weighed tablets of ca. 30 mg of PPh_3. After addition of each tablet the boiling point of the solution was measured. A plot of mol of PPh_3/mol of monomeric 4 (=X) against mol of determined species/mol of monomeric 4 (=Y) shows a straight line to X = 1 with a slope of 0.5, whereafter Y continues to increase linearly to at least X = 3 with a slope of 1.

In Situ Preparation of $[Cu_3\{SC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)\{P(OMe)_3\}]$ (6). To 4 (86 mg, 0.14 mmol) in 0.3 mL of $C_6D_5CD_3$ was added $P(OMe)_3$ (32 μL, 0.28 mmol). At temperatures below 253 K signals of 6 and free 4 were visible in the ^1H NMR spectra in a ratio of 4 to 1. ^1H NMR data are presented in Table IV.

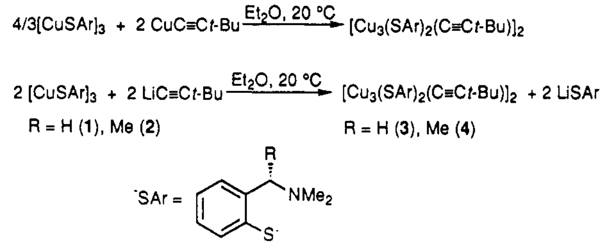
X-ray Structure Determination of $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (3) and $[Cu_3\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ ((*R*)-4). The crystal data and experimental details of the structure determinations are given in Table I. For a full description of the experimental details of the methods used for the structure solution, see Tables S1 and S2 (supplementary material). A crystal of 3 was mounted inside a Lindemann glass capillary in view of its air instability, and a crystal of 4 was glued on top of a glass fiber and transferred to the cold nitrogen stream. It must be noted that the crystal structure determination of 4 was carried out on 4 obtained from the (*R*)-enantiomer of the arenethiolate; vide infra. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections and checked for the presence of higher lattice symmetry.[6] Intensity data were corrected for Lp and absorption (4: DIFABS)[7] and merged into unique sets. The structures were solved with the PATT option of SHELXS86[8] and difference Fourier techniques. Subsequent refinement was done on F by full matrix least-squares methods with SHELX76.[9] Hydrogen atoms were taken into account at calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles. Refinement of the enantiomorphous structure of 4 resulted in higher R-values for the (*S*)-enantiomer in support of the (*R*)-configuration of the material used in the synthesis.

Table I. Crystallographic Data for Compounds 3 and 4

	3[a]	4[b]
formula	$C_{48}H_{66}Cu_6N_4S_4$	$C_{52}H_{74}Cu_6N_4S_4{\cdot}C_4H_{10}O$
a, Å	11.213 (1)	11.600 (2)
b, Å	18.360 (2)	17.071 (3)
c, Å	13.118 (1)	15.513 (3)
β, deg	103.72 (1)	101.53 (1)
V, Å^3	2623.6 (4)	3009.9 (9)
Z	2	2
space group (No.)	$P2_1/c$ (14)	$P2_1$ (4)
T, K	295	100
λ, Å	0.71073	0.71073
d(calc), g cm^{-3}	1.530	1.477
μ, cm^{-1}	25.9	22.6
$R(F)$	0.061	0.056
$R_w(F)$	0.037	0.059

[a] Full data are given in ref 5c. [b] The crystal structure determination was carried out on the compound prepared by starting from the (*R*)-$C_6H_4(CH(Me)NMe_2)$-2 enantiomer.

Scheme I



Final atomic coordinates for the non-hydrogen atoms of 4 are listed in Table II. Neutral scattering factors were taken from Cromer and Mann[10] and corrected for anomalous dispersion.[11] Geometrical calculations, including the thermal motion ellipsoid plots, were done with PLATON.[12] Calculations for 3 were done on a MicroVax-II cluster, and those for 4, on a DEC5000/ULTRIX system.

Results

The reactions of (3,3-dimethyl-1-butynyl)copper with the copper(I) arenethiolates $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (1) as well as enantiomerically pure $[CuSC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2]_3$ (2) in diethyl ether resulted in the selective formation of the neutral 2/1 arenethiolate organocopper compounds $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (3) and $[Cu_3\{SC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (4) in 88 and 76% yield, respectively (Scheme I). In an at-

---

(6) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
(7) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(8) Sheldrick, G. M. SHELXS86. Program for crystal structure determination. University of Göttingen, Göttingen, Federal Republic of Germany, 1986.
(9) Sheldrick, G. M. SHELX76. Crystal structure analysis package. University of Cambridge, Cambridge, England, 1976.
(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(12) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table II. Final Coordinates of the Non-Hydrogen Atoms for 3 and 4

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
			$[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C\equiv C\text{-}t\text{-}Bu)]_2$, (3)				
Cu(1)	0.84345 (13)	0.09337 (8)	0.47441 (11)	C(13)	0.6665 (14)	−0.0057 (9)	0.7853 (10)
Cu(2)	1.07630 (13)	0.02142 (7)	0.59691 (10)	C(14)	0.6351 (13)	0.0525 (8)	0.7170 (10)
Cu(3)	1.03036 (13)	0.10391 (7)	0.40842 (10)	C(15)	0.7187 (13)	0.0868 (8)	0.6732 (9)
S(1)	0.9514 (3)	0.10445 (16)	0.6424 (2)	C(16)	0.6786 (10)	0.1516 (7)	0.6020 (10)
S(2)	1.2119 (3)	0.06495 (15)	0.5016 (2)	C(17)	0.6522 (12)	0.2035 (7)	0.4317 (10)
N(1)	0.6732 (9)	0.1345 (6)	0.4886 (8)	C(18)	0.5737 (10)	0.0831 (7)	0.4477 (9)
N(2)	1.0754 (11)	0.2095 (5)	0.3765 (8)	C(20)	1.2703 (9)	0.1453 (7)	0.5714 (9)
C(1)	0.8627 (11)	0.0801 (7)	0.3313 (11)	C(21)	1.3277 (10)	0.1399 (7)	0.6782 (9)
C(2)	0.8090 (11)	0.0743 (6)	0.2391 (11)	C(22)	1.3799 (12)	0.2019 (9)	0.7293 (11)
C(3)	0.7473 (13)	0.0646 (9)	0.1243 (10)	C(23)	1.3760 (13)	0.2679 (9)	0.6821 (14)
C(4)	0.8235 (13)	0.0996 (8)	0.0570 (9)	C(24)	1.3186 (12)	0.2728 (7)	0.5773 (13)
C(5)	0.6273 (13)	0.1051 (10)	0.1021 (11)	C(25)	1.2670 (11)	0.2126 (7)	0.5212 (11)
C(6)	0.729 (2)	−0.0128 (8)	0.0963 (11)	C(26)	1.2117 (13)	0.2207 (6)	0.4057 (10)
C(10)	0.8400 (11)	0.0632 (7)	0.7000 (10)	C(27)	1.0410 (13)	0.2169 (7)	0.2608 (11)
C(11)	0.8705 (12)	0.0045 (7)	0.7676 (8)	C(28)	1.0167 (12)	0.2655 (6)	0.4221 (11)
C(12)	0.7868 (15)	−0.0295 (8)	0.8120 (10)				
			$[Cu_3\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C\equiv C\text{-}t\text{-}Bu)]_2$ (4)				
Cu(1)	0.15823 (10)	0.31916	0.13265 (8)	C(23)	0.4143 (10)	0.0405 (7)	0.2730 (8)
Cu(2)	0.22372 (11)	0.36172 (12)	0.29691 (8)	C(24)	0.4981 (10)	0.0914 (7)	0.2548 (8)
Cu(3)	0.37668 (11)	0.32782 (11)	0.19269 (8)	C(25)	0.4981 (9)	0.1701 (7)	0.2730 (7)
Cu(4)	0.34896 (12)	0.49385 (11)	0.31339 (9)	C(26)	0.5883 (9)	0.2276 (7)	0.2530 (8)
Cu(5)	0.26403 (11)	0.45925 (11)	0.14752 (8)	C(27)	0.6121 (9)	0.3403 (7)	0.1606 (8)
Cu(6)	0.13123 (11)	0.50469 (11)	0.26454 (8)	C(28)	0.5206 (9)	0.2249 (7)	0.0915 (7)
S(1)	0.0383 (2)	0.32507 (19)	0.22793 (17)	C(29)	0.7065 (10)	0.1861 (8)	0.2483 (9)
S(2)	0.4010 (2)	0.30104 (18)	0.33933 (18)	C(30)	0.4408 (9)	0.6133 (7)	0.2139 (7)
S(3)	0.4500 (2)	0.50919 (19)	0.20166 (18)	C(31)	0.3851 (10)	0.6589 (8)	0.1444 (8)
S(4)	0.1200 (2)	0.55167 (17)	0.12878 (17)	C(32)	0.3821 (11)	0.7382 (8)	0.1532 (10)
N(1)	0.1022 (7)	0.2135 (5)	0.0665 (5)	C(33)	0.4325 (12)	0.7739 (8)	0.2322 (11)
N(2)	0.5364 (7)	0.2724 (6)	0.1721 (6)	C(34)	0.4857 (11)	0.7299 (8)	0.3007 (9)
N(3)	0.4724 (8)	0.5566 (6)	0.4105 (6)	C(35)	0.4961 (9)	0.6490 (7)	0.2936 (8)
N(4)	−0.0408 (9)	0.5420 (6)	0.2839 (6)	C(36)	0.5593 (11)	0.6006 (8)	0.3690 (8)
C(1)	0.2836 (8)	0.3576 (6)	0.0751 (7)	C(37)	0.5285 (12)	0.4931 (9)	0.4674 (9)
C(2)	0.2955 (10)	0.3796 (7)	0.0017 (7)	C(38)	0.4099 (12)	0.6104 (10)	0.4616 (9)
C(3)	0.3128 (12)	0.4110 (9)	−0.0825 (8)	C(39)	0.6548 (11)	0.6420 (9)	0.4342 (9)
C(4)	0.2365 (18)	0.4766 (12)	−0.1120 (12)	C(40)	−0.0200 (9)	0.5091 (6)	0.0855 (6)
C(5)	0.315 (2)	0.3483 (14)	−0.1458 (12)	C(41)	−0.0300 (9)	0.4596 (6)	0.0140 (6)
C(6)	0.4441 (15)	0.4396 (19)	−0.0713 (15)	C(42)	−0.1409 (10)	0.4271 (7)	−0.0242 (8)
C(10)	0.0249 (9)	0.2241 (7)	0.2526 (7)	C(43)	−0.2352 (11)	0.4458 (7)	0.0125 (7)
C(11)	0.0273 (9)	0.2048 (8)	0.3427 (8)	C(44)	−0.2259 (9)	0.4914 (7)	0.0833 (7)
C(12)	0.0182 (10)	0.1275 (8)	0.3672 (8)	C(45)	−0.1187 (9)	0.5265 (6)	0.1226 (7)
C(13)	0.0103 (9)	0.0683 (8)	0.3070 (8)	C(46)	−0.1066 (10)	0.5815 (7)	0.2017 (8)
C(14)	0.0074 (10)	0.0874 (7)	0.2190 (8)	C(47)	−0.0076 (11)	0.5998 (8)	0.3546 (8)
C(15)	0.0131 (9)	0.1644 (6)	0.1904 (7)	C(48)	−0.1067 (10)	0.4785 (8)	0.3142 (8)
C(16)	−0.0038 (9)	0.1767 (6)	0.0917 (7)	C(49)	−0.2222 (10)	0.6192 (8)	0.2080 (8)
C(17)	0.0781 (10)	0.2295 (8)	−0.0295 (7)	C(51)	0.2201 (9)	0.4635 (7)	0.3769 (7)
C(18)	0.1998 (9)	0.1576 (7)	0.0873 (7)	C(52)	0.2117 (10)	0.4432 (7)	0.4508 (8)
C(19)	−0.1178 (9)	0.2212 (7)	0.0568 (7)	C(53)	0.2021 (12)	0.4194 (8)	0.5397 (8)
C(20)	0.4060 (9)	0.2001 (7)	0.3105 (6)	C(54)	0.262 (3)	0.3453 (16)	0.5613 (14)
C(21)	0.3195 (9)	0.1472 (7)	0.3307 (7)	C(55)	0.2414 (16)	0.4867 (10)	0.6055 (9)
C(22)	0.3237 (10)	0.0696 (7)	0.3110 (8)	C(56)	0.0742 (16)	0.4020 (11)	0.5421 (9)

tempt to obtain neutral heterocuprates of the type $CuLi_n(SAr)(C\equiv C\text{-}t\text{-}Bu)_n$ (SAr = $SC_6H_4(CH(R)NMe_2)\text{-}2$; R = H, Me), (3,3-dimethyl-1-butynyl)lithium was reacted with the copper(I) arenethiolates 1 or 2 in diethyl ether. Surprisingly, from these reactions the organocopper arenethiolates 3 and 4 were also obtained instead of the expected heterocuprates (Scheme I); in this case 3 and 4 could be isolated in only moderate yields (±45% based on 1 or 2) due to the formation of soluble lithium arenethiolates.

Compound 3 dissolves in CH_2Cl_2 while 4 is also soluble in benzene and $CHCl_3$. Both 3 and 4 can be crystallized from dichloromethane solutions. As solids, 3 and 4 are stable in air for weeks, but their solutions exposed to air decompose within minutes. Ebulliometric molecular weight measurements of 3 and 4, in dichloromethane, showed a concentration-dependent molecular weight. At low concentrations (17.25 g/L) the aggregation state is close to trinuclear (monomeric) $[Cu_3(SAr)_2(C\equiv C\text{-}t\text{-}Bu)]$, while at higher concentrations (44.1 g/L) it is close to being hexanuclear (dimeric) $[Cu_3(SAr)_2(C\equiv C\text{-}t\text{-}Bu)]_2$. In the infrared spectra of 3 and 4 there is no absorption band attributable to an acetylide $\nu(C\equiv C)$ in the region 1900–2200 cm^{-1}.

Addition of at least 2 equiv of a phosphine or a phosphite to a suspension of 3 in benzene or diethyl ether results in a clear solution. An ebulliometric titration experiment of 3 with PPh_3 in CH_2Cl_2 indicated that triphenylphosphine reacts with 3 to give a trinuclear unit with only one phosphine ligand coordinated, i.e. $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C\equiv C\text{-}t\text{-}Bu)(PPh_3)]$ (**5**) (eq 1).

$$[Cu_3(SAr)_2(C\equiv C\text{-}t\text{-}Bu)]_2 + 2L \rightleftarrows 2[Cu_3(SAr)_2(C\equiv C\text{-}t\text{-}Bu)L] \quad (1)$$

Excess phosphine does not coordinate. Attempts to isolate 5 by crystallization failed; hexanuclear 3 and PPh_3 crystallize out. This result indicates that 3 and PPh_3 are in equilibrium with 5. N-donor ligands, such as acetonitrile, pyridine, and triethylamine, and carbon monoxide do not react with 3 and 4. For example, the CO infrared stretching frequency for coordinated CO was not found when CO was bubbled through a solution of 3 or 4. Sim-

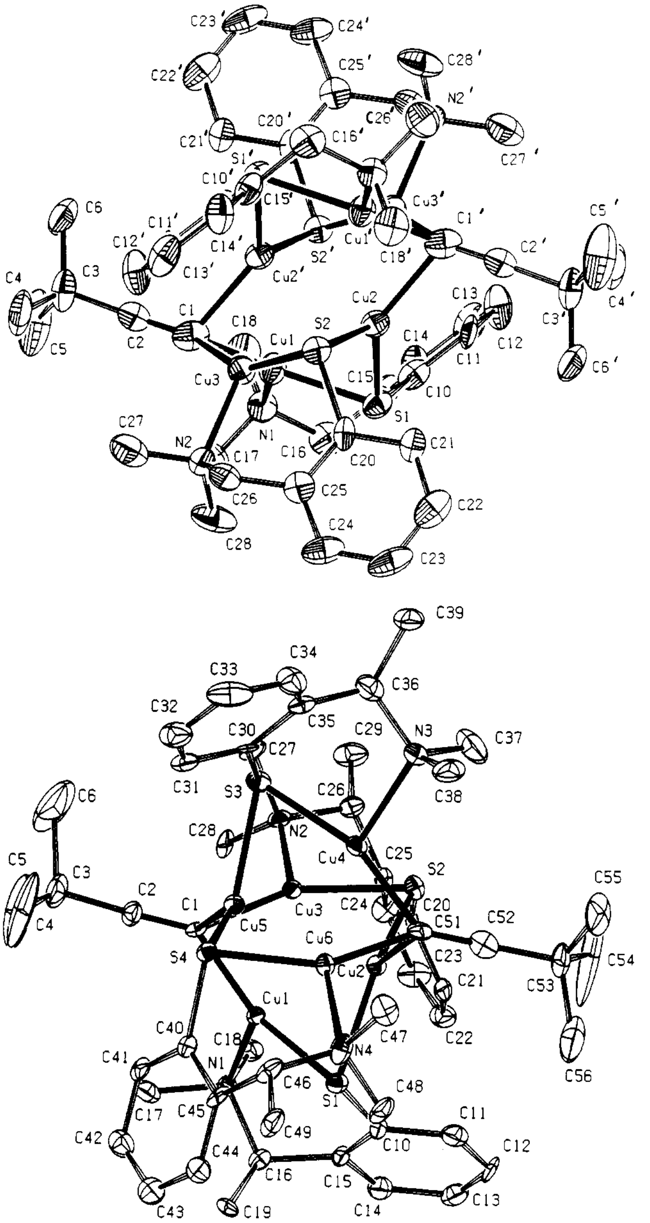


Figure 1. ORTEP drawings with the atom-labeling schemes of (top) $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (**3**) (30% probability level) and (bottom) $[Cu_3\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (**4**) (40% probability level).

ilarly ethene was not able to dissolve **3** in benzene. NMR and molecular weight determinations (procedure as for PPh_3; see Experimental Section) showed that the enone PhCH=CHC(O)Ph does not complex with **3** or **4** to any measurable degree. In boiling toluene, **3** and **4** are inert to benzylideneacetone.

To investigate the aggregation state of these hetero-organocopper compounds further, the molecular structures of **3** and **4** in the solid state were determined by X-ray single-crystal diffraction studies. The ORTEP drawing of **3** and **4** and the adopted numbering schemes are shown in Figure 1, and a list of relevant bond distances and angles is given in Table III. Both compounds consist of two trinuclear copper units, $[Cu_3(SAr)_2(C{\equiv}C\text{-}t\text{-}Bu)]$, in which neighboring copper atoms are bridged by either an arenethiolate or an alkynyl group. The three copper atoms, the two sulfur atoms, and the bridging carbon atom of the alkynyl group together form a six-membered Cu_3S_2C ring which is in a boatlike conformation. This is in contrast to the Cu_3S_3 ring in the starting compounds, **1** and **2**, which is in a chair conformation.[5a] In the trinuclear unit the copper atoms Cu(1) and Cu(3) that are bridged by C(1) of the alkynyl group are each also coordinated by an ortho amino function of an arenethiolato group (see Figure 2); consequently, the chelating arms do not describe a "turn" around the copper array as in **1** and **2**. The other copper atom Cu(2) of the trinuclear unit is bonded to two sulfur atoms that bridge between this atom and Cu(1) and Cu(3). Through side-on coordination of the bridging alkynyl group of one unit to the coordinatively unsaturated copper atom Cu(2) of a second unit a hexanuclear structure is formed.

In the $Cu_3(SAr)_2(C{\equiv}C\text{-}t\text{-}Bu)$ units, where C(1) and Cu(2) are the prow atoms of the boat conformation, there are three configurational isomers possible based on axial

Table III. Important Bond Distances (Å) and Bond Angles (deg) in $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (3) and $[Cu_3\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)]_2$ (4)[a]

	3	4[b]	
C(1)–C(2)	1.22 (2)	1.23 (2)	1.22 (2)
Cu(1)–C(1)	1.96 (1)	1.96 (1)	1.97 (1)
Cu(2)–C(1′)	2.13 (1)	2.14 (1)	2.10 (1)
Cu(3)–C(1)	1.96 (1)	1.99 (1)	2.01 (1)
Cu(2)–C(2′)	2.84 (1)	2.79 (1)	2.73 (1)
Cu(1)–N(1)	2.10 (1)	2.112 (8)	2.15 (1)
Cu(3)–N(2)	2.07 (1)	2.160 (9)	2.17 (1)
Cu(2)–S(1)	2.245 (3)	2.290 (3)	2.316 (3)
Cu(2)–S(2)	2.327 (3)	2.279 (3)	2.274 (3)
Cu(1)–S(1)	2.258 (3)	2.225 (3)	2.293 (3)
Cu(3)–S(2)	2.229 (3)	2.282 (3)	2.233 (3)
Cu(1)·Cu(3)	2.458 (2)	2.523 (2)	2.494 (2)
Cu(1)·Cu(2′)	2.555 (2)	2.677 (2)	2.667 (3)
Cu(2)·Cu(3′)	2.587 (2)	2.673 (3)	2.620 (3)
Cu(1)·Cu(2)	3.026 (2)	2.612 (2)	2.632 (2)
Cu(2)·Cu(3)	2.841 (2)	2.691 (2)	2.718 (2)
Cu(2)·Cu(2′)	2.819 (2)	2.966 (2)	
S(1)–S(2)	3.877 (5)	4.237 (4)	3.838 (4)
S(1)–S(2′)	3.867 (4)	5.799 (4)	5.945 (4)
Cu(1)–S(1)–Cu(2)	84.4 (1)	70.69 (8)	69.65 (9)
Cu(1)–S(1)–C(10)	96.2 (4)	101.1 (4)	89.0 (4)
Cu(2)–S(1)–C(10)	111.7 (4)	106.2 (4)	109.4 (4)
Cu(2)–S(2)–Cu(3)	77.1 (1)	72.33 (9)	74.2 (1)
Cu(2)–S(2)–C(20)	102.5 (4)	116.1 (4)	110.8 (4)
Cu(3)–S(2)–C(20)	101.1 (4)	87.0 (3)	94.9 (3)
Cu(1)–C(1)–Cu(3)	77.7 (5)	79.3 (4)	77.5 (4)
Cu(1)–C(1)–Cu(2′)	77.4 (5)	82.2 (4)	79.8 (4)
Cu(2′)–C(1)–Cu(3)	78.4 (5)	79.5 (4)	81.0 (4)
S(1)–Cu(1)–N(1)	99.7 (3)	100.9 (2)	95.9 (3)
S(1)–Cu(1)–C(1)	142.4 (4)	154.7 (3)	160.0 (3)
N(1)–Cu(1)–C(1)	116.1 (5)	104.4 (4)	104.0 (4)
S(1)–Cu(2)–S(2)	116.0 (1)	136.0 (1)	113.5 (1)
S(1)–Cu(2)–C(1′)	129.3 (4)	111.5 (3)	107.8 (3)
S(2)–Cu(2)–C(1′)	110.9 (4)	108.8 (3)	131.2 (3)
S(2)–Cu(3)–N(2)	100.2 (3)	96.9 (3)	98.2 (3)
S(2)–Cu(3)–C(1)	148.2 (4)	154.3 (3)	152.2 (3)
N(2)–Cu(3)–C(1)	110.7 (5)	107.5 (4)	108.4 (4)
C(1)–C(2)–C(3)	177 (1)	176 (1)	180 (1)

[a] Uncertainties in the last significant digit are shown in parentheses. [b] Corresponding distances and angles in related trinuclear parts of **4**.

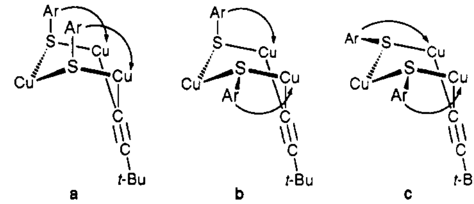


Figure 2. Schematic views of trinuclear (monomer) $Cu_3(SAr)_2(C{\equiv}C\text{-}t\text{-}Bu)$ units (SAr = $SC_6H_4(CH(R)NMe_2)\text{-}2$; R = H, Me) showing different possible positions of the aryl groups on the sulfur atoms with respect to the boatlike Cu_3S_2C ring: (a) all axial; (b) equatorial and axial; (c) all equatorial.

Table IV. ^{1}H NMR (200 MHz)^a Data for [Cu$_3${SC$_6$H$_4$(CH$_2$NMe$_2$)-2}$_2$(C≡C-*t*-Bu)]$_2$ (**3**), [Cu$_3${SC$_6$H$_4$((*S*)-CH(Me)NMe$_2$)-2}$_2$(C≡C-*t*-Bu)]$_2$ (**4**), and [Cu$_3${SC$_6$H$_4$((*S*)-CH(Me)NMe$_2$)-2}$_2$(C≡C-*t*-Bu){P(OMe)$_3$}] (**6**)

	T (K)	*t*-Bu (s)	CMe (d)	NMe$_2$ (s)	CH/CH$_2$ (q)/(s/d)	Ar *o*-H (dd)	Ar (m)
3	293	1.51		2.41	3.35	7.71	6.85–7.05
	193	1.46		1.99, 2.30, 2.47, 2.62	2.81 (2×), 3.40, 3.71	7.51, 7.89	6.85–7.15
4	313	1.44	1.44	2.36	3.73	7.58	6.90 (s)
	223	1.47, 1.56	1.20, 1.23, 1.24, 1.43	2.07, 2.13, 2.30, 2.40, 2.54, 2.62, 2.74, 2.86	2.76, 4.16, 4.51, 4.54, 3.34	7.70, 7.90, 7.91, 7.98	6.0–7.2
6^b	353	1.29	1.46	2.28	3.57	7.76	6.75–6.95
6^c	233	1.24	0.95	1.90, 2.29	2.9, 4.3	8.06	6.6–7.2

^{a} δ in ppm relative to TMS. Solvents: **3** in CD$_2$Cl$_2$, **4** in CDCl$_3$, and **6** in C$_6$D$_5$CD$_3$. ^{b} P(OMe)$_3$ doublet at 3.43 ppm with *J*(H,P) = 12.9 Hz. ^{c} P(OMe)$_3$ doublet at 3.37 ppm with *J*(H,P) = 12.9 Hz.

or equatorial positioning of the aryl groups on the sulfur atoms with respect to the Cu$_3$S$_2$C ring (see Figure 2). In both trinuclear units in **3**, one of the aryl groups is bound in the equatorial and the other in the axial position (Figure 2b). In **4**, one trinuclear unit is like those in **3**, but in the other unit all aryl groups are axially positioned (Figure 2a). The third possibility of two equatorially positioned aryl groups (Figure 2c) is not found in **3** and **4** but has been found in [Cu$_3$(SAr)$_2$(Mes)(PPh$_3$)].[13]

In **3** and **4** the coordination geometries of the copper atoms are planar (and $\sum_{\text{angles}}$ = 353–360°); the copper atoms Cu(1) and Cu(3) have an approximate T-shaped surrounding of one sulfur, one carbon, and one nitrogen atom, while the other, Cu(2), is trigonally coordinated by two sulfur atoms and the alkynyl function of the second Cu$_3$(SAr)$_2$(C≡C-*t*-Bu) unit. All sulfur atoms are tricoordinate with the coordination sites being occupied by two copper atoms and one carbon atom; there is also a stereochemically active lone pair present. The Cu–S–Cu angles are acute (69.6–84.4°), and this indicates that the atoms of the Cu$_2$S moiety are united by an electron-deficient two-electron three-center (2e-3c) bond with an sp^2-hybridized sulfur atom; this type of bonding was earlier proposed by us for **1** and **2**.[5a]

The Cu–S bond lengths in both **3** and **4** fall in the expected range 2.22–2.33 Å for sulfur coordinated to tricoordinate copper atoms.[5a] In the Cu$_3$S$_2$C ring the Cu(1)–C(1) and Cu(3)–C(1) bond distances of 1.96–2.02 Å, the small Cu–C–Cu bond angle of 77.5–79.3°, and the Cu(1)···Cu(3) distances of 2.458–2.523 Å are normal for a 2e-3c Cu$_2$C bonding situation. However, the overall bonding of the C$^\alpha$≡C$^\beta$-*t*-Bu unit (C(1)≡C(2)-*t*-Bu) in the hexanuclear compound is unusual. The C≡C function from one monomeric unit is side-on coordinated to Cu(2′) of the second unit so affording a long Cu(2′) to C$^\alpha$ bond distance (2.10 (1)–2.14 (1) Å) and an even longer Cu(2′) to C$^\beta$ distance of 2.73–2.84 Å. This results in Cu(1)···Cu(2′) and Cu(3)···Cu(2′) distances of 2.555–2.677 Å. This unprecedented bonding mode of the alkynyl group to three copper atoms in **3** and **4** is discussed later.

It would appear in **4** that the axial positioning of the three aryl groups allows some reduction of steric interactions between the trinuclear units that would be present if all aryl groups were to be positioned as in **3**. However the consequence of this is that there is now a sterically and energetically unfavorable orientation of one of the benzylic methyl groups in the plane of the aromatic ring.[14]

The ^{1}H NMR (200 MHz) spectra of both **3** (CD$_2$Cl$_2$) and **4** (CDCl$_3$) were measured with a concentration high enough (>100 g/L) to have principally hexanuclear (dimeric) species present. At room temperature the spectrum of **3** displays one signal for the *t*-Bu group and one signal pattern for the arenethiolate groups (see Table IV). When the solution of **3** is cooled to 253 K, all signals broaden and the *N*-methyl groups decoalesce into two broad singlets ($\Delta\nu$ = 78 Hz; T_c = 270 K; $\Delta G^\ddagger$ = 53 kJ mol^{-1}). On further cooling to 193 K, one sharp signal for the *t*-Bu group remains, but two arenethiolate group patterns are present in a 1:1 ratio (data for the ortho aromatic protons: $\Delta\nu$ = 76 Hz; T_c = 230 K; $\Delta G^\ddagger$ = 45 kJ mol^{-1}) with, instead of two, four signals for the *N*-methyl groups ($\Delta\nu$ = 30 Hz; T_c = 235 K; $\Delta G^\ddagger$ = 48 kJ/mol; $\Delta\nu$ = 62 Hz; T_c = 244 K; $\Delta G^\ddagger$ = 48 kJ/mol). The temperature-dependent processes are reversible, and this indicates that **3** is fluxional.

It is likely that, at low temperature (193 K) and with the concentration used, **3** has the same hexanuclear structure in solution as in the solid state. On the basis of the latter, in which the two Cu$_3$(SAr)$_2$(C≡C-*t*-Bu) units are fully equivalent, one expects only two ligand patterns for the SAr groups in the low-temperature NMR spectrum, and this is what is found. Since four *N*-methyl groups are present, it can be concluded that the Cu–N bond is stable on the NMR time scale. A likely rationale for the SAr exchange process seen is an inversion of configuration at the sulfur atoms (the aryl goes from the equatorial position to the axial position and back; $\Delta G^\ddagger$ = 45–48 kJ mol^{-1}).[5a] The best explanation for the methyl group exchange is based on a copper-nitrogen dissociation/association process ($\Delta G^\ddagger$ = 53 kJ mol^{-1}) with inversion of configuration at the nitrogen atom.[15]

The same processes observed for **3** also take place in **4**, but the assignment of the NMR signals is more complicated due to lower symmetry in **4** that results from the extra methyl group on the benzylic carbon of the SAr group. The signals of the low-temperature (223 K) ^{1}H NMR spectrum of **4** could be assigned with the help of a ^{1}H,^{1}H COSY phase-sensitive 2D experiment.[16] At this temperature, eight *N*-methyl signals, four SAr ligand patterns, and two singlet signals for two different *t*-Bu groups are seen. This is to be expected if the structure in solution is the same as that found in the solid state. At room temperature (293 K), the signals for the *t*-Bu groups have coalesced into one signal ($\Delta\nu$ = 17 Hz; T_c = 255 K; $\Delta G^\ddagger$ = 53 kJ/mol), the signals for the *N*-methyl groups have coalesced into two broad signals and there are two broad SAr ligand patterns. The signals from the *t*-Bu groups can only become isochronous if the molecule con-

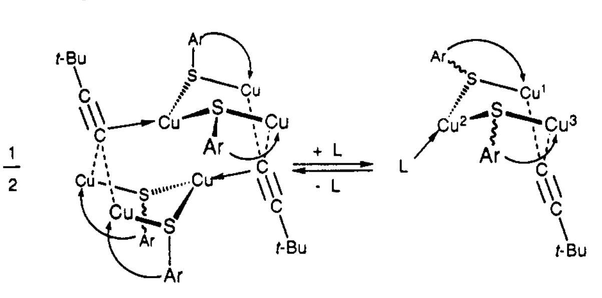
---

[13] Knotter, D. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400.

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

[15] The inversion of configuration at the sulfur center alone cannot render the amino-methyl groups equivalent. This can occur only when a process involving Cu–N bond dissociation with concomitant pyramidal N-inversion as well as rotation around the C–N bond followed by Cu–N coordination takes place. Nitrogen inversion is a low-energy process of ±26 kJ/mol: Bushweller, C. H.; Wang, C. Y.; Reny, J.; Lourandos, M. Z. *J. Am. Chem. Soc.* **1977**, *99*, 3938.

[16] (a) Abbreviations and techniques used in the text include the following: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; COSY = correlation spectroscopy; Eyring equation, $\Delta G^\ddagger = -RT_c \ln[2\pi h(\Delta\nu)/kT_c\sqrt{3}]$ with $\Delta G^\ddagger$ = free energy of activation (J); T_c = coalescence temperature (K); $\Delta\nu$ = chemical shift difference (Hz); other symbols have their usual meaning. (b) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.



3 R = H
4 R = Me

5 R = H; L = PPh_3
6 R = Me; L = $P(OMe)_3$

Figure 3. Reaction of phosphine ligands with 3 and 4 with the formation of trinuclear 5 and 6.

tains a rotation axis as its pseudosymmetry element. This pseudorotation axis evolves when inversion of the configuration of the sulfur atom occurs. Consequently, each SAr on one monomeric unit becomes isochronous with one SAr group of the other monomeric unit. So far the fluxional process is the same as that observed for 3 and has the same $\Delta G^{\ddagger}$. However, above room temperature the two SAr ligand patterns of 4 coalesce into one (benzylic protons: $\Delta\nu$ = 180 Hz; T_c = 305 K; $\Delta G^{\ddagger}$ = 58 kJ/mol). This is a fluxional process which gives 4 a second pseudorotation symmetry axis perpendicular to the first one and which involves dissociation of the hexanuclear structure and conformation flips of the Cu_3S_2C ring (see Discussion). Due to the complexity of the ^1H NMR spectra of 4, we could not measure the exact concentration dependence of this $\Delta G^{\ddagger}$.

The variable-temperature ^1H NMR spectra of 5 are difficult to assign because of the complex aryl region, and this compound has not been studied further. However, the compound $[Cu_3\{SC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2\}_2(C{\equiv}C\text{-}t\text{-}Bu)\{P(OMe)_3\}]$ (6), prepared in situ in $C_6D_5CD_3$ from 4 and 2 equiv. of $P(OMe)_3$, is more easily studied by ^1H NMR. The hexanuclear dimer 4 and phosphine complex 6 (see Figure 3) are present at 233 K in a 1 to 4 ratio. The interpretation of ^1H NMR signals at 353 K (the fast-exchange limit) is straightforward (see Table IV). The $P(OMe)_3$ ligand is coordinated to copper since its chemical shift is 0.11 ppm to high field of that of free $P(OMe)_3$ and the $^3J(H,P)$ is 3 Hz larger than in free $P(OMe)_3$. The *t*-Bu group of 6 remains as one singlet over the whole temperature range studied (353–213 K). Since hexanuclear (dimeric) 4 displays two singlets for the *t*-Bu groups in the low-exchange limit, these data indicate that 6 is a trinuclear species. Complex 6 has one aromatic ligand pattern present from 353 to 213 K. While there are two *N*-methyl group signals at 233 K at higher temperatures, there is only one (T_c = 250 K; $\Delta\nu$ = 78 Hz; $\Delta G^{\ddagger}$ = 49 kJ/mol). At lower temperatures (213 K) the *N*-methyl group signals broaden and decoalesce into four singlets ($\Delta G^{\ddagger}$ = ±40 kJ/mol). The fluxionality of the *N*-methyl groups is a two-step process. One step is Cu–N dissociation/association with a $\Delta G^{\ddagger}$ value of 49 kJ/mol, and the other, lower energy step, involves conformational changes of the trinuclear units (see Discussion).

Discussion

Preparation. The selective substitution of one arenethiolate group in $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (1) and $[CuSC_6H_4((S)\text{-}CH(Me)NMe_2)\text{-}2]_3$ (2) for one alkynyl group, so forming 3 and 4 selectively, was unexpected. In particular we anticipated that the reaction of alkynyllithium with 1 and 2 would provide heterocuprates. Apparently, 3 and 4 are very stable with respect to other organocopper species or organocuprates which could have been formed. We propose that this selective formation of 3 and 4 is due to the capability of the alkynyl group to give side-on coordination and act as a supplementary two-electron donor. However, while the substitution of arenethiolate groups in 1 and 2 with alkynyllithium stops at an early stage, the reaction of 2 with bis(mesityl)magnesium has been shown to afford a complete exchange of arenethiolates for mesityl groups and formation of $[CuMes]_4[\mu\text{-}SAr]_2[MgSAr]_2$.[13,17] Although in solution this latter compound is present as mixture of species, addition of a phosphine ligand does lead to the specific formation of one organocopper compound, i.e. $[Cu_3(SAr)_2(Mes)(L)]$ (L = PPh_3).[13] This compound is related to the complexes $[Cu_3(SAr)_2(C{\equiv}C\text{-}t\text{-}Bu)(L)]$ (5 and 6), which result from the reaction of 4 and 5 with PPh_3 and $P(OMe)_3$, respectively, but which could not be isolated. In this reaction the dimer breaks up into monomeric units with one coordinated phosphine ligand. To achieve this, the bonding between the monomeric units, i.e. the interaction of the alkynyl group in one unit to a copper center in another, is broken and the phosphine coordinates to the vacant coordination site (see Figure 3). The occurrence of this reaction is consistent with the C≡C side-on coordination mode of the alkynyl group in 3 and 4.

Bonding Description. The reason that the alkynylcopper arenethiolates 3 and 4 are hexanuclear, whereas the pure copper arenethiolates 1 and 2 are trinuclear, has a plausible explanation when the number of valence electrons is taken into account. In 1 and 2 each arenethiolato group donates four electrons (two from the amine group and two from the sulfur atom; cf. the 2e-3c bonding description for the SAr monoanion in ref 5a) and occupies three coordination sites (one by the amine group and two by the bridging S atom) so affording three equivalent trigonally coordinated copper sites. However, compared to those in 1 and 2, the copper atoms in trinuclear (monomeric) units in 3 and 4 have two valence electrons less as one four-electron-donating arenethiolate group is substituted by a two-electron-donating alkynyl group. Moreover, one copper atom is coordinately unsaturated because the alkynyl group occupies only two coordination sites. Consequently, the Cu_3 unit in 3 and 4 is electrophilic and can bind a further two-electron-donating ligand. This can be either the C≡C group of a second monomeric Cu_3 unit, leading to dimerization and the formation of the observed hexanuclear compound, or an external phosphine ligand, leading to trinuclear 5 and 6.

Before considering where the trinuclear unit takes up the electron-donating ligand, it is necessary to consider the exact coordination of the arenethiolate groups as found in the X-ray structures of 3 and 4. In these structures we find that the amine groups coordinate to the copper atoms involved in the two-electron three-center bond with the alkynyl group. Obviously these copper atoms are harder Lewis acids than the unique copper atom, Cu(2), involved in bonding to two sulfur atoms, which are soft Lewis bases. As a consequence, in both 3 and 4 Cu(2) is a coordinatively unsaturated copper center with a soft Lewis acid character, and it is at this site that soft Lewis bases (like phosphines and the C≡C group of another trinuclear unit) coordinate. Hard Lewis bases, like amines, do not coordinate to this copper center, which makes the chemistry of 3 to 6 an interesting example of fine-tuning. Through the choice of the ligands used, weak and hard Lewis acidic sites can be created on an organocopper cluster in such a way that a substrate molecule with a certain Lewis basicity can specifically bond to the required copper site.

---

(17) Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1990**, *112*, 5895.

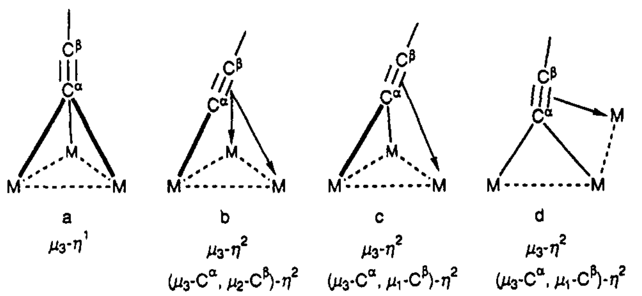


Figure 4. Possible bonding modes of one alkynyl group to three metal centers.

Bonding of the Alkynyl Group. Many organometallic compounds containing alkynyl or isoelectronic carbonyl and isonitrile groups have been prepared, and structural characterization has shown them to have a broad spectrum of possible bonding modes. The alkynyl group in **3** and **4** has interactions to three copper atoms, and the bonding is of a type unprecedented for these isoelectronic ligands. (A summary of the known modes is to be found in Figure 4[18]). In **3** and **4** the $C^\alpha{\equiv}C^\beta$-*t*-Bu group is positioned so that C^α bridges over all three atoms (μ_3-C^α), with the very similar Cu(1)–C^α and Cu(3)–C^α distances being significantly shorter than the Cu(2′)–C^α distance. The alkynyl function is so orientated that it is side-on bonded to Cu(2′) with C^β fairly close to this one copper atom (μ_1-C^β). This bonding type (μ_3-C^α,μ_1-C^β)-η^2 [19] (Figure 4c) is fairly symmetrical since there is an approximate mirror plane passing through Cu(2′), C^α, and C^β that is perpendicular to the Cu(1)···Cu(3) vector. In the literature there is one example of a very asymmetric (μ_3-C^α,μ_1-C^β)-η^2 bonding mode in which all interacting atoms lie in the same plane (Figure 4d).[20]

Side-on coordination of alkynyl groups in organocopper complexes generally gives rise to a longer distance from the metal atom to the β-carbon than to the α-carbon (see supplementary Table S4).[13,14] This is because the cationic copper atom prefers bonding to the α-carbon, which has higher electron density than C^β, and this leads to nonsymmetrical or "slipped alkynyl" bonding. In **3** and **4** the Cu(2)–C^α distance is normal for this type of bonding, but the Cu(2)–C^β distance is extremely long (2.84 (1) Å). We propose that the steric bulk of the *t*-Bu group may be a secondary factor that is accentuating the asymmetric coordination of the alkynyl group.

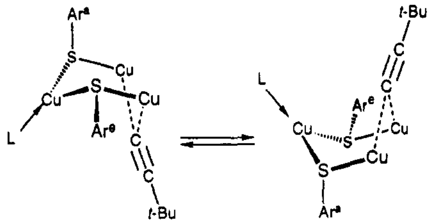


Figure 5. Schematic representation of the boat-to-boat conformation flip (no inversion of configuration at sulfur) of [$Cu_3\{SC_6H_4((S)$-$CH(Me)NMe_2)$-$2\}_2(C{\equiv}C$-*t*-Bu)$\{P(OMe)_3\}$] (**6**).

Fluxional Processes. Compounds **3** and **4** in solution, and in the concentration range where the predominant species present is hexanulcear (dimeric $Cu_3(SAr)_2(C{\equiv}C$-*t*-Bu) units), are subject to a number of fluxional processes. Inversion of configuration at the sulfur atoms ($\Delta G^\ddagger$ = 45–48 kJ mol^{-1}) and a copper–nitrogen dissociation/association process ($\Delta G^\ddagger$ = 53 kJ mol^{-1}) were mentioned earlier and can explain their ^{1}H NMR coalescence patterns from 213 to 293 K. However, to explain the spectra of **4** at higher temperatures (second rotation axis as a pseudosymmetry element), it is necessary to invoke a further two-step fluxional process ($\Delta G^\ddagger$ = 58 kJ/mol) that most likely involves a dimer–monomer equilibrium. If the lifetime of the monomeric unit is long enough, then fast boat-to-boat conformation flipping can give rise to a pseudosymmetry element in the monomeric unit (a rotation axis) as the two SAr ligands flip between axial and equatorial positions and become isochronous (see Figure 5). Accordingly, the $\Delta G^\ddagger$ value found is for the dimer–monomer equilibrium, i.e. breaking of the side-on alkynyl to copper interactions, rather than for the boat-to-boat flip, which is expected to be a lower energy process.

The ^{1}H NMR spectra of the monomeric trinuclear compound [$Cu_3\{SC_6H_4((S)$-$CH(Me)NMe_2)$-$2\}_2(C{\equiv}C$-*t*-Bu)$\{P(OMe)_3\}$] (**6**) provide us with more information on the boat-to-boat flip process. Over a large temperature range monomeric **6** shows one ligand pattern and this indicates that the compound contains a pseudorotation axis as a symmetry element. Observing the signals of the *N*-methyl groups, one sees that fluxional processes (Cu–N bond dissociation/association) could be stopped on the NMR time scale at temperatures lower than 250 K. Spectral changes in the range 210–240 K indicate a second lower energy process ($\Delta G^\ddagger$ = ±40 kJ/mol), but although decoalescence to four *N*-methyl signals occurred, the slow-exchange limit was not reached. The relatively low $\Delta G^\ddagger$ is appropriate for a boat-to-boat conformation flip, which is independent of inversion of configuration at sulfur; the latter is a higher energy process ($\Delta G^\ddagger \geq$ 48 kJ/mol).

Because the arenethiolate $SC_6H_4((S)$-$CH(Me)NMe_2)$-2 in **6** contains a specific chiral center, then the aryl groups can only become isochronous via a boat-to-boat conformation flip if one aryl group is in axial and the other in an equatorial position with respect to Cu_3S_2C ring (see Figure 5). A boat conformation with both aryl groups equatorial (or axial) has no mirror plane symmetry, and this would provide two ligand patterns until the point where inversion of configuration of sulfur occurs—this is not the case.

Conclusions

The trinuclear copper unit [$Cu_3\{SC_6H_4(CH(R)NMe_2)$-$2\}_2(C{\equiv}C$-*t*-Bu)] can be considered as a model for reactive $Cu_3(SAr)_2R'$ species which are present in "cuprate" solutions made from $[CuSAr]_3$ and organometallic reagents

---

[18] Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.

[19] Herrmann, W. A.; Biersack, H.; Ziegler, M. L.; Weidenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.

[20] Corfield, W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *21*, 957.

[21] (a) Otsuka, S.; Okura, N.; Otsuka, S. *J. Am. Chem. Soc.* **1983**, *105*, 245. (b) Pasquali, M.; Leoni, P.; Floriani, C.; Manfredotti, A. G. *Inorg. Chem.* **1982**, *21*, 4324. (c) Thompson, J. S.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 5488. (d) Maier, G.; Hoppe, M.; Reisenauer, H. P.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 437. (e) Villacorta, G. M.; Gibson, D.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6732. (f) Clark, R.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2027. (g) Abu-Salah, O. M.; Al-Ohaly, A. R. A.; Knobler, C. B. *J. Chem. Soc., Chem. Commun.* **1985**, 1502. (h) Carriedo, G. A.; Miguel, D.; Riera, V.; Solans, X.; Font-Altaba, M.; Coll, M. *J. Organomet. Chem.* **1986**, *299*, C43. (i) Raghavan, N. V.; Davis, R. E. *J. Cryst. Mol. Struct.* **1976**, *6*, 73. (j) Solans, X.; Solans, J.; Miravitlles, C.; Miguel, D.; Riera, V.; Rubio-Gonzalez, J. M. *Acta Crystallogr.* **1986**, *42*, 975. (k) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1974**, *13*, 1418. (l) Abu-Salah, O. M.; Bruce, M. I.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1974**, 855. (m) ten Hoedt, R. W. M.; Noltes, J. G.; van Koten, G.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1800. (n) Corfield, W. R.; Gainsford, G. J. *Am. Cryst. Assoc., Abst.* **1970**, 83. (o) Naldini, L.; DeMartin, F.; Manassero, M.; Sansoni, M.; Rassu, G.; Zoroddu, M. A. *J. Organomet. Chem.* **1985**, *279*, C42. (p) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Solans, X. *J. Organomet. Chem.* **1988**, *346*, 277. (q) Drew, M. G. B.; Esho, F. S.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1982**, 1347. (r) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aquirre, A.; Garcia-Granda, S. *J. Organomet. Chem.* **1989**, *378*, C11.

Organometallics 1992, 11, 4090–4096

(LiR′ or MgR′X), i.e. wherein one or two Cu centers are replaced by Li or MgX. The trinuclear unit has a reactive site to which we anticipate that the alkene function of enones would coordinate, i.e. the initial reaction step proposed for their copper(I)-catalyzed reaction with organometallic reagents.[13,22,23] This coordination does not occur in $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C\equiv C\text{-}t\text{-}Bu)]$ since the strength of the side-on alkynyl to copper bond favors a hexanuclear structure. However, with phosphines as two-electron donors, trinuclear compounds $[Cu_3\{SC_6H_4(CH(R)NMe_2)\text{-}2\}_2(C\equiv C\text{-}t\text{-}Bu)\{P(OMe)_3\}]$ are formed.

Four fluxional processes in hexanuclear and trinuclear alkynylcopper arenethiolates have been observed. In order of increasing free energy of activation energy ($\Delta G^{\ddagger}$), these are the boat-to-boat conformation flip of the Cu_3S_2C ring (±40 kJ/mol), inversion of configuration at sulfur and Cu–N dissociation (both ±50 kJ/mol), and hexanuclear to trinuclear dissociation via breaking of the side-on alkynyl to copper interactions (±58 kJ/mol).

Acknowledgment. This work was supported in part (A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). The X-ray data were collected by Mr. A. J. M. Duisenberg.

Supplementary Material Available: For **3** and **4**, tables of fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal parameters (23 pages). Ordering information is given on any current masthead page.

OM920150L

---

(22) (a) Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988**, *60*, 57. (b) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063.

(23) Lambert, F.; Knotter, D. M.; Janssen, M. D.; Van Klaveren, M.; Boersma, J.; Van Koten, G. *Tetrahedron: Asymmetry* **1991**, *2*, 1097.

Synthesis and Characterization of Mononuclear Pyrazolyl Complexes of Palladium(II) and Platinum(II). Crystal Structures of $[NBu_4][M(C_6F_5)_2(pyrazole)(pyrazolato)]$ (M = Pd, Pt)

Gregorio López,*[†] José Ruiz,[†] Consuelo Vicente,[†] José M. Martí,[†] Gabriel García,[†]
Penny A. Chaloner,[‡] Peter B. Hitchcock,[‡] and Robin M. Harrison[‡]

Departamento de Química Inorgánica, Universidad de Murcia, 30071 Murcia, Spain,
and School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Received April 21, 1992

Pyrazolyl complexes of the types $[MR_2(HX)_2]$ (M = Pd, R = C_6F_5, HX = pyrazole (Hpz) (**1**), 3,5-dimethylpyrazole (Hdmpz) (**2**); M = Pd, R = C_6Cl_5, HX = Hpz (**3**), Hdmpz (**4**); M = Pt, R = C_6F_5, HX = Hpz (**5**), Hdmpz (**6**); M = Pt, R = C_6Cl_5, HX = Hdmpz (**7**)) and $[NBu_4][M(C_6F_5)_2Cl(Hpz)]$ (M = Pd (**8**), Pt (**9**)) have been prepared by reaction of *cis*-$[MR_2(PhCN)_2]$ and $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}Cl)\}_2]$, respectively, with HX (1:2 mole ratio). Deprotonation by NBu_4OH of complexes **1**, **3**, and **5**, and **6** leads to the formation of the pyrazole–pyrazolato complexes $[NBu_4][MR_2X(HX)]$ (M = Pd, X = pz, R = C_6F_5 (**10**), C_6Cl_5 (**11**); M = Pt, R = C_6F_5, X = pz (**12**), dmpz (**13**); M = Pt, R = C_6Cl_5, X = pz (**14**)). The IR and NMR data for complexes **10**–**14** show that both pyrazolyl ligands are identical, and the X-ray structure determinations of **10** and **12** have established the existence of a intramolecular hydrogen bond between the two pyrazolyl rings, the coordination at palladium and platinum being essentially square planar. The structures are isomorphous, and both compounds are tetragonal, space group $P4_32_12$. Crystal data for **10**: $a = b = 17.022$ (2) Å, $c = 12.466$ (3) Å, $Z = 4$, 2146 reflections, $R = 0.045$. Crystal data for **12**: $a = b = 17.088$ (2) Å, $c = 12.466$ (4) Å, $Z = 4$, 2540 reflections, $R = 0.029$.

Introduction

Pyrazole-type heterocycles represent an important class of ligands in organometallic chemistry,[1-3] and the coordination chemistry of these ligands has been the subject of an excellent review by Trofimenko.[1] They can act as neutral monodentate (pyrazole-*N*), anionic monodentate (pyrazolato-*N*), or exo-bidentate anionic ligands (pyrazolato-*N*,*N*′) on coordination to metal centers.

The syntheses of a number of organometallic binuclear nickel, palladium, and platinum complexes of the types $[R_2M(\mu\text{-}X)_2MR_2]^{2-}$, $[R_2M(\mu\text{-}OH)(\mu\text{-}X)MR_2]^{2-}$, and $[R(PPh_3)M(\mu\text{-}OH)(\mu\text{-}X)M(PPh_3)R]$ (R = C_6F_5, C_6Cl_5, $C_6H_2F_3$-2,4,6; X = exo-bidentate pyrazolate-type ligand; M = Ni,[4,5] Pd,[6-9] Pt[10]) have been reported recently. Nonorganometallic pyrazolato palladium and platinum complexes of general formula $[(L\text{-}L)MX_2]$ (L-L = various bis(diphenylphosphines) and bis(diphenylarsines), 2,2′-

---

[†] University of Murcia.

[‡] University of Sussex.

(1) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

(2) Steel, P. J. *Coord. Chem. Rev.* **1990**, *106*, 227.

(3) Elguero, J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: New York, 1984; Vol. 5, p 167.

(4) López, G.; García, G.; Ruiz, J.; Sánchez, G.; García, G.; Vicente, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1045.

(5) López, G.; García, G.; Sánchez, G.; García, J.; Ruiz, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518.

(6) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabó, J.; Molins, E.; Miravitlles, G. *Inorg. Chem.* **1991**, *30*, 2605.

(7) López, G.; García, G.; Sánchez, G.; Santana, M. D.; Ruiz, J.; García, J. *Inorg. Chim. Acta* **1991**, *188*, 195.

(8) López, G.; Ruiz, J.; García, G.; Martí, J. M.; Sánchez, G.; García, J. *J. Organomet. Chem.* **1991**, *412*, 435.

(9) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Santana, M. D. *J. Organomet. Chem.* **1990**, *393*, C53.

(10) López, G.; Ruiz, J.; García, G.; Vicente, C.; Rodríguez, V.; Sánchez, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1681.

0276-7333/92/2311-4090$03.00/0