4.1-5.5 (m, 8 H), 6.8-7.2 (m, 2 H), 7.3-7.56 (m, 1 H), 7.6-7.76 (m, 1 H); UV (nm) 304, 258 (inflection), 248, 242; mass spectrum, m/e 606 (100 M + 1), 605 (44 M^+), 562 (13, M - CH_3CO), 648 (17, M + CH_3CO); fluorescence, apple green; forms red complex when treated with $FeCl_3$ which distributes into $CHCl_3$ in $CHCl_3/H_2O$ system.

HPLC analysis [Alltech 600 RP 8 column (25 cm × 0.25 in.) eluting with H_2O/MeOH (1:1) at 1.2 mL min^{-1} and detecting with a Beckman analytical optical unit at 254 nm]: two peaks with retention times 3.58 min and 4.56 min. Only the later peak was obtained when the mycobactin was first dissolved in CH_2Cl_2, shaken with dilute aqueous $FeCl_3$ to convert it to the ferric complex, and an aliquot of the CH_2Cl_2 layer subjected to HPLC analysis.

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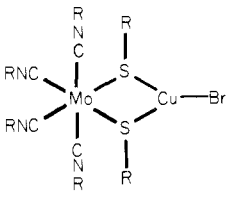
Synthesis and X-ray Structures of the Conformational Isomers of the Mixed Bimetal Complex $(t\text{-BuNC})_4Mo(\mu\text{-}t\text{-BuS})_2CuBr$

Nicholas C. Payne,[1a] Nobuyuki Okura,[1b] and Sei Otsuka*[1b]

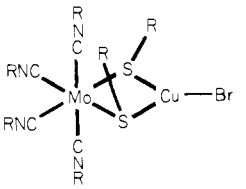
Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560. *Received March 17, 1982*

Abstract: The molecular fragment *cis*-$Mo(t\text{-BuS})_2$ has been found to act as a bidentate ligand, exhibiting affinity toward d^{10} metals. Reaction of $Mo(t\text{-BuS})_4$ or *cis*-$(Mo(t\text{-BuS})_2(t\text{-BuNC})_4$ with $CuBr(t\text{-BuNC})_3$ in acetone under dinitrogen gives crystals of formula $(t\text{-BuNC})_4Mo(\mu\text{-}t\text{-BuS})_2CuBr$. Two isomers have been isolated in the solid state, differing only in the relative arrangements of the *tert*-butyl substituents on the thiolato bridges. The anti-upright isomer **1** crystallizes from an acetone–toluene mixture with a molecule of diphenylacetylene in a monoclinic cell of dimensions a = 11.702 (2), b = 20.134 (4), and c = 10.455 (4) Å, β = 98.85 (2)°, Z = 2, and space group $P2_1$. Refinement by block-diagonal least-squares methods on F using 3690 unique, diffractometer data converged at R = 0.09. Compound **1** contains a MoS_2Cu core, with Mo–Cu = 2.628 (2) Å. The Mo atom has a distorted octahedral coordination geometry, with a large S–Mo–S angle of 105 (1)°. The Cu atom has almost ideal trigonal-planar geometry. A second isomer, **2**, may be crystallized from acetone in the orthorhombic space group *Pnma*, cell dimensions a = 21.994 (2), b = 16.411 (3), and c = 10.605 (1) Å, with Z = 4. Full-matrix least-squares refinement on F using 2882 averaged data converged at R = 0.08. m symmetry is imposed upon the molecule, which differs from **1** only in that the t-Bu substituents on the thiolato bridges adopt a syn-upright conformation. The interconversion of **1** and **2** has been demonstrated by variable-temperature ^1H NMR, and values of $\Delta G^\ddagger$ = 7.1 (7) kcal mol^{-1}, $\Delta H^\ddagger$ = 4.9 (2) kcal mol^{-1}, and $\Delta S^\ddagger$ = -6 (2) cal mol^{-1} deg^{-1} estimated for the conformational change.

Recently a number of bridged and unbridged molybdenum dimeric complexes have been prepared. Mixed-metal dinuclear compounds containing a molybdenum atom as one component, however, still remain a rarity.[2] The incentive for the present preparation of Mo–Cu complexes originated from the known antagonistic function of molybdenum ion against copper in ruminants.[3] Several types of Mo–Cu polymeric compounds have been prepared by Müller and his group, employing mainly MoS_4^{2-} as the source of the Mo component.[4] We have been interested in the interaction of thiolate ligand containing molybdenum species with Cu atoms. Since the reactive $Mo(t\text{-BuS})_4$[5] and other molybdenum 2-methyl-2-propanethiolate compounds[6] such as $Mo^{II}(t\text{-BuS})_2(t\text{-BuNC})_4$[7] were available, we have first examined interactions of these species with Cu(I) or Cu(II) ions. This study has led to the preparation of the novel title compound. Serendipitously we have isolated two conformational isomers in the solid state, differing only in the arrangements of the t-Bu substituents on the bridging thiolato ligands, namely anti-upright (**1**), and syn-upright (**2**). Their syntheses and single-crystal X-ray structure analyses are described herein.



1



2

R = t-Bu

Experimental Section

Materials. $Mo(t\text{-BuS})_4$[5] and $Mo(t\text{-BuS})_2(t\text{-BuNC})_4$[7] were prepared according to the procedures described previously. All solvents were dried

(1) (a) On leave from Chemistry Department, University of Western Ontario, London, Ontario, N6A 5B7, Canada. (b) Osaka University.

(2) (a) Coucouvanis, D.; Simhon, E. D.; Swenson, D.; Baenziger, N. C. *J. Chem. Soc., Chem. Commun.* **1979**, 361-362. (b) Coucouvanis, D.; Baenziger, N. C.; Simhon, E. D.; Stremple, P.; Swenson, D.; Kostikas, A.; Simopoulos, A.; Petrouleas, V.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1980**, *102*, 1730-1732.

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Table I. Crystal Data and Experimental Conditions

	isomer 1	isomer 2
formula	$C_{42}H_{64}BrCuMoN_4S_2$	$C_{28}H_{54}BrCuMoN_4S_2$
formula weight	928.51	750.25
a, Å	11.702 (2)	21.994 (2)
b, Å	20.134 (4)	16.411 (3)
c, Å	10.455 (4)	10.605 (1)
β, deg	98.85 (2)	
cell volume, Å^3	2433.9	3827.9
crystal system	monoclinic	orthorhombic
systematic absences	$0k0$, k odd	$hk0$, h odd; $0kl$, $k + l$ odd
space group	$P2_1$	*Pnma*
Z	2	4
density, calcd, g cm^{-3}	1.266	1.301
density, obsd, g cm^{-3}	1.23 (1)	1.31 (1)
neutral buoyancy in	CCl_4–C_6H_{12}	CCl_4–C_6H_{14}
μ(Cu K$\bar{\alpha}$), cm^{-1}	48.2	46.1
λ(Cu K$\bar{\alpha}$), Å	1.54178	1.54178
radiation, prefilter	Cu, Ni	Cu, Ni
take-off angle	2°	2°
aperture, distance	5 × 5 mm, 40 cm	5 × 5 mm, 40 cm
data collected	$\pm h, \pm k, l$	$+h, \pm k, +l$
scan width	1.4°, dispersion corrected	1.4°, dispersion corrected
scan speed	4° min^{-1}	4° min^{-1}
background	5.5 s	5.5 s
standards	002, 040, 231, 300, $0\bar{4}0$ every 100 observations	060, 222, 402, 600, $0\bar{6}0$ every 100 observations

and deaerated by distillation under a nitrogen atmosphere.

Physical Measurements. Spectroscopic measurements were made by instruments described in the previous paper.[5]

Preparation of Bis(μ-2-methyl-2-propanethiolato)bromotetrakis(*tert*-butyl isocyanide)molybdenum copper (t-BuNC)$_4$Mo(μ-t-BuS)$_2$CuBr (2). Mo(t-BuS)$_4$ (499 mg, 1.1 mmol) and CuBr(t-BuNC)$_3$[8] (431 mg, 1.1 mmol) were dissolved in acetone (50 mL) under dinitrogen. The dark red color of Mo(t-BuS)$_4$ rapidly turned into a bright carmine, and the solution was stirred for 3 h at ambient temperature. The solution was filtered, and the filtrate was concentrated in vacuo. After cooling at −5 °C overnight, the concentrate gave crimson crystals (496 mg, 60% yield on the basis of Mo(t-BuS)$_4$). The crystals (mp 180 °C dec) were fairly soluble in acetone but only poorly so in toluene. Generally the crystalline sample formed directly from the reaction mixture was found to be analytically pure. Anal. Calcd for $C_{28}H_{54}N_4BrS_2MoCu$: C, 44.82; H, 7.25; N, 7.47; Br, 10.65. Found; C, 44.81; H, 7.15; N, 7.45; Br, 10.85. Crystals of **2** were also formed upon cooling to room temperature a hot (ca. 50 °C) acetone–toluene solution of the solid product formed in the above reaction. However, if the product precipitation was effected by adding toluene to a cold acetone solution made by dissolving the crystals of **2** at room temperature, the product was an amorphous powder whose IR spectrum was different from that of **2** (see Results).

Alternatively, a mixture of Mo(t-BuS)$_2$(t-BuNC)$_4$ (141 mg, 0.23 mmol) and CuBr(t-BuNC)$_3$ (92 mg, 0.23 mmol) in acetone (10 mL) was stirred at room temperature. After concentration, filtration, and cooling, the reaction mixture gave the crimson compound **2** in over 30% yield.

Preparation of Bis(μ-2-methyl-2-propanethiolato)bromotetrakis(*tert*-butyl isocyanide)molybdenum copper–diphenylacetylene (t-BuNC)$_4$Mo-(μ-t-BuS)$_2$CuBr·$C_6H_5C{\equiv}CC_6H_5$ (1). A mixture of $C_6H_5C{\equiv}CC_6H_5$ (35 mg, 0.20 mmol) and **2** (90 mg, 0.12 mmol) was heated in refluxing acetone (10 mL) for 1 h. The brownish-lake solution was cooled to ambient temperature and filtered, and the filtrate was then concentrated in vacuo. After the solution stood overnight at −5 °C, the concentrate gave crimson crystals (39 mg, 35% yield), mp 143 °C dec. Anal. Calcd for $C_{42}H_{64}N_4BrS_2MoCu$: C, 54.33; H, 6.95; N, 6.03; Br, 8.61. Found: C, 54.09; H, 6.89; N, 6.06; Br, 8.88. The crystals of **1** were also obtained upon cooling (−5 °C) an acetone–toluene or acetone solution of a mixture of **2** and an excess of diphenylacetylene, prepared at room temperature.

X-ray Diffraction Study of Mo(μ-t-BuS)$_2$CuBr·$C_6H_5C{\equiv}CC_6H_5$ (1). Blocky, crimson colored crystals of **1** were recrystallized from an acetone–toluene mixture and mounted in capillaries under a dry N_2 atmosphere. Preliminary cell dimensions and space group were determined from Weissenberg and precession photography. Systematic absences (Table I) were consistent with either space group $P2_1$ (no. 4) or $P2_1/m$ (no. 11).[9a] In the latter case, either m or $\bar{1}$ site site symmetry is imposed; only the former is possible for this molecule. The crystal density, measured by the flotation method, indicated two formula units per cell.

Intensity data were collected from a crystal of approximate dimensions 0.40 × 0.29 × 0.19 mm, with faces {010}, {001}, and {100} in point group 2 (vide infra) by using monochromatic Cu radiation from a Rigaku-Denki Rotaflex rotating anode X-ray generator and a Rigaku-Denki AC5 diffractometer. Accurate cell dimensions and an orientation matrix at 19 °C were refined by employing the angular settings for 24 reflections with $33 < 2\theta < 49°$. The crystal mosaicity was adequate; ω scans of some low-angle intense reflections had a mean width at half-height of 0.18°. Bijvoet pairs were recorded out to a 2θ maximum of 120° by the θ–2θ scan technique to resolve the space group ambiguity. Five standard reflections, monitored regularly as a check on crystal and electronic stability, showed an average linear decay of 2.5%. No correction was made for this. Stationary crystal, stationary counter background measurements were made at the scan limits. Attenuators were employed for intense reflections. In all, 8075 observations were measured. Details of data collection and crystal data are given in Table I.

The raw data were corrected for background radiation, Lorentz and polarization corrections applied, and standard deviations $\sigma(F_o)$ assigned by using the program library at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. An absorption correction was made by using the North–Phillips method;[10] transmission factors varied by 56%. An inspection of the Bijvoet pairs $I(hkl)$ and $I(\bar{h}kl)$ suggested the acentric space group. Thus, averaging the 225 symmetry related reflection pairs $h0l$ and $\bar{h}0l$ gave an agreement factor $R = 2.8\%$, whereas agreement between the Bijvoet pairs gave $R = 4.5\%$. These data were therefore not averaged, and the structure was solved and refined in space group $P2_1$ by using 3690 unique data ($\pm h,k,l$) with $I > 0$. A successful refinement later confirmed this choice.

The structure was solved with the direct methods program MULTAN[11] and, owing to restrictions on computer core, refinement of atomic parameters was by block-diagonal least-squares methods on F. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight w is given by $1.0/(\sigma(F_o) - 0.780|F_o| + 0.035|F_o|^2)$. Neutral atom scattering factors were taken from the International Tables, Volume IV,[9b] and real and imaginary contributions were included for all atoms.[12] Anisotropic thermal parameters were assigned to all 51 non-hydrogen atoms, and refinement converged at agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.092$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.097$, 3690 observations and 459 variables. An inspection of the structure at this stage showed good agreement between chemically equivalent dimensions. However the *tert*-butyl groups were showing considerable thermal motion, and some possibility of disorder also exists. As a result, we were unable to include the 54 hydrogen atoms in the refinement. These factors undoubtedly

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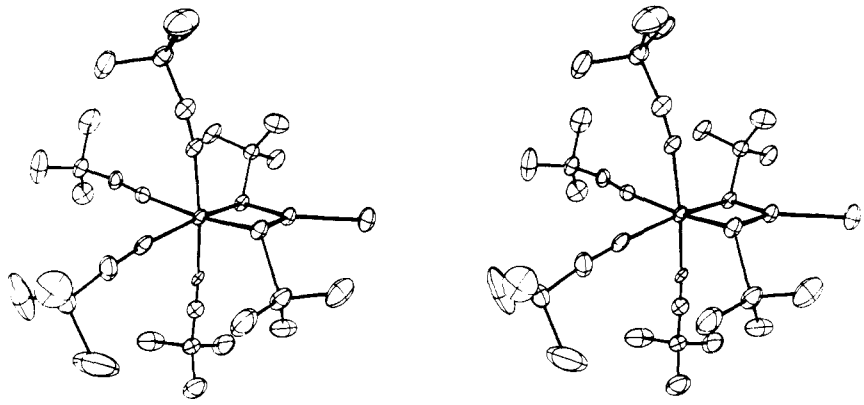

Figure 1. Stereoview of the anti-upright isomer **1**.

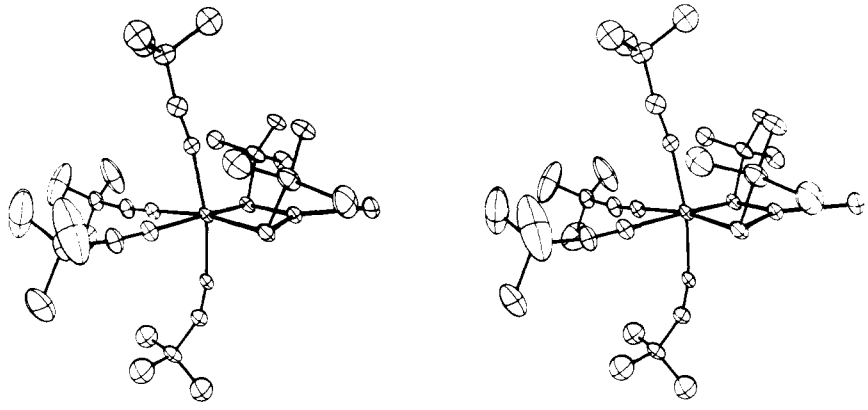

Figure 2. Stereoview of the syn-upright isomer **2**.

contribute to the relatively high residual. Inversion of the structure in a mirror at $y = 0$ and refinement under identical conditions gave only partial convergence, agreement factors $R_1 = 0.099$ and $R_2 = 0.106$, and a model with chemically equivalent distances that differed significantly due to polar dispersion error. The original model was therefore considered proven. The error on an observation of unit weight is 3.5 electrons. A total difference Fourier synthesis showed no significant residual electron density, and there was no evidence for extinction. Final positional parameters are given in Table II, and structure amplitudes are listed in the supplementary material.[13]

X-ray Diffraction Study of (*t*-BuNC)$_4$Mo(μ-*t*-BuS)$_2$CuBr (2). The X-ray analysis of **2** was carried out with only minor changes to the procedures employed for **1**. Accordingly, only differences will be described.

Crimson blocks were obtained by recrystallization from acetone. A photographic examination showed orthorhombic symmetry, and systematic absences indicated space groups *Pnma* (no. 62) or $Pn2_1a$ (alternative setting of $Pna2_1$, no. 33).[9a] The crystal density was consistent with $Z = 4$, which imposes *m* symmetry in the former and no symmetry in the latter space group. Intensity data were collected from a crystal of approximate dimensions 0.47 × 0.27 × 0.17mm, with faces of the forms {010}, {011}, and {110} in point group *mmm* (vide infra). ω scans of intense, low-angle reflections had a mean width of 0.17°. Bijvoet pairs hkl and $h\bar{k}l$ were recorded out to a 2θ maximum of 120°, giving a total of 5951 observations. The standard reflections showed only random fluctuations during data collection. An absorption correction[10] was applied to the data; transmission coefficients varied by 19.7%. Averaging of 252 symmetry-related reflection pairs gave an agreement factor $R = 0.014$; averaging the 2581 Bijvoet pairs gave $R = 0.017$. This evidence suggested the centric space group *Pnma*, with *m* symmetry imposed upon the molecule, and all subsequent calculations were in this space group using 2882 averaged observations with $I > 0$. The structure was solved by a combination of Patterson and Fourier techniques and refined by full-matrix least-squares methods on F. The weight w is given by $1.0/(\sigma(F_o) + 0.150|F_o| + 0.005|F_o^2|)$. Anisotropic thermal parameters were assigned to all atoms except the methyl carbon atoms of the *tert*-butyl groups lying on the mirror plane, since attempts to refine them resulted

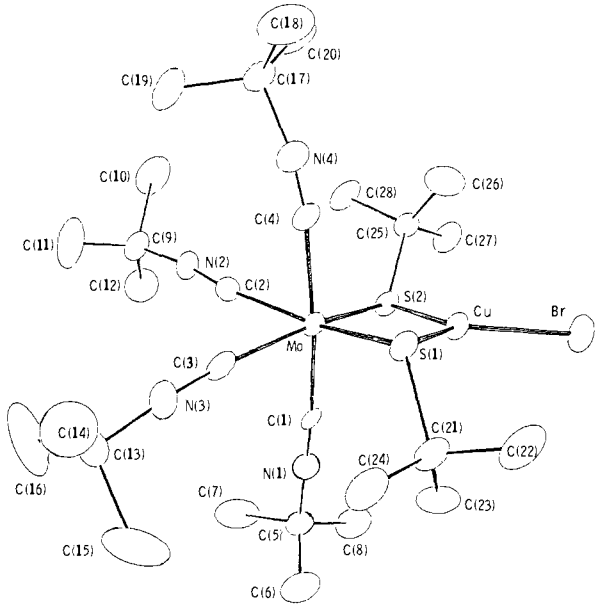

Figure 3. Anti-upright isomer **1** showing the atom numbering scheme.

in nonpositive definite values. In a difference Fourier synthesis, clear evidence was found for disorder of C(6) and C(7), and C(18) and C(19). Several models were tried to account for this, but the most acceptable was also the simplest, with isotropic thermal parameters applied to each atom. High B values resulted ranging from 13.3 (6) to 18 (1) Å^2, but the fragment geometries were close to tetrahedral. As in the case of **1**, the molecular dimensions were entirely acceptable, though considerable thermal motion was found for the *tert*-butyl groups. For this reason we were unable to include the 22 unique hydrogen atoms. The structure refinement converged at values of $R_1 = 0.08$ and $R_2 = 0.12$, with 2882 observations and 197 variables. The error on an observation of unit weight is 1.2 electrons. A final difference Fourier synthesis showed no important residual electron density, and there was no evidence for sec-

(13) Supplementary material; Table V and VI in supplementary material only.

Table II. Positional ($\times 10^4$) Parameters for 1

atom	x	y	z
Mo	1688.4 (6)	0	8792.2 (7)
Br	2248 (2)	-2195.5 (7)	6862 (2)
Cu	1942 (1)	-1161.7 (8)	7729 (2)
S(1)	3313 (2)	-376 (1)	7819 (3)
S(2)	310 (2)	-905 (1)	8498 (3)
N(1)	2200 (11)	-635 (6)	11689 (11)
N(2)	-286 (9)	1040 (5)	9455 (11)
N(3)	3323 (10)	1189 (6)	10243 (11)
N(4)	1030 (10)	847 (5)	6174 (11)
C(1)	2021 (9)	-430 (5)	10653 (10)
C(2)	418 (11)	665 (6)	9314 (12)
C(3)	2639 (9)	766 (5)	9686 (12)
C(4)	1247 (9)	505 (5)	7022 (11)
C(5)	2447 (12)	-884 (7)	12986 (12)
C(6)	3682 (17)	-894 (12)	13469 (23)
C(7)	1777 (20)	-419 (18)	13787 (18)
C(8)	1938 (23)	-1604 (10)	13059 (27)
C(9)	-1087 (13)	1518 (7)	9797 (14)
C(10)	-2050 (12)	1594 (10)	8538 (26)
C(11)	-475 (19)	2182 (9)	9940 (25)
C(12)	-1655 (18)	1228 (15)	10975 (21)
C(13)	4015 (15)	1619 (7)	11060 (17)
C(14)	4828 (17)	1952 (13)	10104 (22)
C(15)	5082 (38)	1116 (15)	11827 (39)
C(16)	3373 (29)	2062 (20)	11809 (42)
C(17)	484 (10)	1339 (6)	5240 (12)
C(18)	1326 (24)	1437 (11)	4216 (22)
C(19)	506 (30)	1981 (9)	6036 (23)
C(20)	-655 (15)	1078 (10)	4576 (19)
C(21)	4653 (10)	-711 (6)	8821 (17)
C(22)	5237 (12)	-1071 (9)	7801 (18)
C(23)	4438 (14)	-1151 (10)	9824 (14)
C(24)	5405 (16)	-148 (9)	9239 (23)
C(25)	-865 (9)	-912 (6)	7122 (12)
C(26)	-376 (14)	-869 (9)	5833 (16)
C(27)	-1469 (15)	-1581 (8)	7203 (19)
C(28)	-1682 (9)	-321 (8)	7257 (16)
C(30)	3982 (12)	2495 (9)	6564 (16)
C(31)	4672 (13)	1986 (8)	6126 (15)
C(32)	5575 (15)	2118 (8)	5521 (15)
C(33)	6265 (15)	1618 (10)	5086 (16)
C(34)	6001 (16)	932 (8)	5355 (16)
C(35)	5078 (19)	785 (9)	5953 (22)
C(36)	4447 (14)	1305 (9)	6378 (16)
C(40)	3514 (15)	2925 (10)	6950 (18)
C(41)	2770 (15)	3481 (10)	7410 (15)
C(42)	2972 (15)	4132 (10)	7031 (17)
C(43)	2349 (17)	4647 (12)	7584 (16)
C(44)	1548 (18)	4453 (13)	8484 (24)
C(45)	1407 (23)	3786 (14)	8664 (22)
C(46)	1917 (21)	3303 (13)	8197 (23)

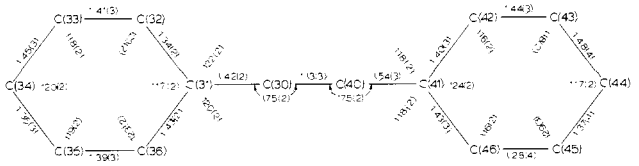

Figure 4. Intramolecular dimensions within the diphenylacetylene molecule, cocrystallized with isomer **1**.

ondary extinction. Final positional parameters are given in Table III, and thermal parameters and structure amplitudes are listed in the supplementary material.[13]

Some selected structural parameters are summarized in Tables IV–VI,[13] and stereoscopic views of complexes **1** and **2** are shown in Figures 1 and 2, respectively, drawn with 40% probability thermal ellipsoids.[14] The atom numbering scheme for **1** given in Figure 3 has also been used for **2** to permit a ready comparison of the two compounds. The intramolecular dimensions of the PhC≡CPh molecule in the crystals of **1** are shown in Figure 4.

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Table III. Positional ($\times 10^4$) Parameters for 2

atom	x	y	z
Mo	1616.5 (3)[a]	1/4	7447.8 (8)
Br	258.8 (7)	1/4	9982 (2)
Cu	650.7 (7)	1/4	8885 (2)
S(1)	1095.0 (8)	3665 (1)	8306 (2)
N(1)	1097 (5)	1/4	4583 (12)
N(2)	2602 (3)	3773 (4)	6248 (8)
N(4)	2538 (5)	1/4	9794 (10)
C(1)	1233 (5)	1/4	5661 (11)
C(2)	2259 (4)	3330 (5)	6672 (8)
C(4)	2155 (5)	1/4	9032 (11)
C(5)	847 (7)	1/4	3307 (13)
C(6)	158 (18)	1/4	3295 (35)
C(7)	987 (9)	3259 (14)	2660 (18)
C(9)	2992 (4)	4332 (6)	5555 (11)
C(10)	3568 (9)	4458 (17)	6314 (21)
C(11)	3211 (13)	3953 (16)	4426 (22)
C(12)	2643 (9)	5058 (14)	5272 (33)
C(17)	3158 (5)	1/4	10254 (14)
C(18)	3144 (19)	1/4	11682 (36)
C(19)	3463 (9)	3232 (14)	9719 (19)
C(21)	544 (4)	4255 (5)	7316 (10)
C(22)	266 (5)	4843 (7)	8218 (15)
C(23)	59 (4)	3705 (6)	6727 (10)
C(24)	918 (5)	4663 (8)	6249 (13)

[a] Estimated standard deviations correspond to the least significant digits.

Results

Preparation and Properties. The reaction of dark red Mo(*t*-BuS)$_4$ (**4**) with CuBr(*t*-BuNC)$_3$ in acetone occurs readily at ambient temperature to give a bright carmine solution from which was isolated a crimson dinuclear complex of formula MoCuBr(*t*-BuS)$_2$(*t*-BuNC)$_4$ (**2**) in a substantial yield (60%). This compound was also obtained from Mo(*t*-BuS)$_2$(*t*-BuNC)$_4$ (**3**) and CuBr(*t*-BuNC)$_3$. When compound **2** was mixed with an excess of PhC≡CPh in acetone–toluene or acetone, a crystalline product of similar color was formed in a form different from that of **2**. The elemental analysis of the purified crystals gave a formula corresponding to a tolane adduct, MoCuBr(*t*-BuS)$_2$(*t*-BuNC)$_4$C$_6$H$_5$C≡CC$_6$H$_5$ (**1**). They are moderately stable toward air and thermally stable. Unexpectedly, the ^{1}H NMR spectrum of **2** (Table VII) was very similar to that of **1**. Complex **1** shows no spectroscopic indication of coordination of the acetylene, e.g., no IR absorption in the region 1900–1600 cm^{-1}. In fact, as revealed by the present X-ray analysis, the tolane molecule in **1** has no bonding interaction with the MoCu moiety but merely acts as a crystalline molecule in the unit cell (vide infra). The X-ray diffraction studies confirmed the existence of two conformational isomers in the solid state, anti-upright **1** and syn-upright **2**, with respect to the thiolate *tert*-butyl groups.

Syn compound **2** is characterized by strong IR N≡C stretching bands at 2140 and 1960 cm^{-1}, whereas anti compound **1** has no IR absorption at 1960 cm^{-1}, but instead the phenyl bands at 762 and 693 cm^{-1} (Table VII) are prominent. The distinction between **1** and **2** thus can be conveniently made on the basis of the absence (**1**) or presence (**2**) of the 1960-cm^{-1} band. The amorphous sample obtained upon addition of toluene to an acetone solution of **2** prepared at room temperature showed an IR feature in the N≡C stretching region that appears to be comprised of the spectra of **1** and **2**.

Their ^{1}H NMR spectra in acetone were almost identical. The temperature-variant behavior was then studied on a chlorobenzene solution of **2**, prepared at room temperature. At 27 °C, five *tert*-butyl proton signals of the isocyanide ligands are observable, suggesting the existence of both conformational isomers in solution (Figure 5). Note that there should be two types of *t*-BuNC ligands in **1** and three types in **2**. Consistently there are two *tert*-butyl proton signals assignable to the *tert*-butyl thiolate ligands. Upon raising the temperature, these two ^{1}H signals coalesce at about 70 °C, as do the signals due to the *t*-BuNC ligands. Above 70 °C only three ^{1}H signals can be observed. The energetics

Table IV. Selected Intramolecular Dimensions

	1	2
	Bond, Å	
Mo-S(1)	2.410 (3)	2.409 (2)
Mo-S(2)	2.415 (3)	
Mo-C(1)	2.10 (1)	2.07 (1)
Mo-C(2)	2.12 (1)	2.127 (9)
Mo-C(3)	2.07 (1)	
Mo-C(4)	2.09 (1)	2.06 (1)
Cu-Br	2.317 (2)	2.314 (2)
Cu-S(1)	2.234 (3)	2.233 (3)
Cu-S(2)	2.244 (3)	
S(1)-C(21)	1.89 (2)	1.87 (1)
S(2)-C(22)	1.81 (1)	
C(1)-N(1)	1.18 (2)	1.18 (2)
N(1)-C(5)	1.39 (2)	1.46 (2)
C(2)-N(2)	1.17 (2)	1.14 (1)
N(2)-C(9)	1.46 (2)	1.46 (2)
C(3)-N(3)	1.23 (2)	
N(3)-C(13)	1.37 (2)	
C(4)-N(4)	1.15 (2)	1.17 (2)
N(4)-C(17)	1.49 (2)	1.45 (2)
	Angle, deg	
S(1)-Mo-S(2)	105.0 (1)	105.1 (1)
C(2)-Mo-C(3)	76.4 (5)	79.6 (3)
S(1)-Mo-C(3)	91.2 (4)	88.0 (3)
S(2)-Mo-C(2)	91.5 (4)	
C(1)-Mo-C(4)	174.1 (4)	168.8 (5)
S(1)-Mo-C(2)	158.8 (4)	
S(2)-Mo-C(3)	159.1 (4)	
C(1)-Mo-C(3)	83.2 (5)	
C(2)-Mo-C(4)	81.4 (5)	86.2 (4)
C(1)-Mo-C(2)	92.7 (5)	85.2 (4)
C(3)-Mo-C(4)	95.0 (5)	
S(1)-Cu-S(2)	117.5 (1)	117.8 (1)
Br-Cu-S(1)	120.1 (1)	121.1 (1)
Br-Cu-S(2)	122.4 (1)	
Mo-S(1)-Cu	68.8 (1)	68.4 (1)
Mo-S(2)-Cu	68.6 (1)	
Mo-S(1)-C(21)	121.8 (6)	120.4 (3)
Mo-S(2)-C(25)	120.8 (4)	
Cu-S(1)-C(21)	107.1 (6)	108.3 (3)
Cu-S(2)-C(25)	107.5 (4)	
Mo-C(1)-N(1)	177 (1)	171 (1)
Mo-C(2)-N(2)	173 (1)	179.5 (8)
Mo-C(3)-N(3)	173 (1)	
Mo-C(4)-N(4)	171 (1)	170 (1)
C(1)-N(1)-C(5)	179 (1)	173 (1)
C(2)-N(2)-C(9)	173 (1)	172 (1)
C(3)-N(3)-C(13)	170 (1)	
C(4)-N(4)-C(17)	165 (1)	156 (1)

of the anti ⇄ syn upright conformational change were estimated by employing a site-exchange rate expression for the temperature region above coalescence.[15] Values of $\Delta G^{\ddagger}$ = 7.1 (±0.7) kcal mol^{-1}, $\Delta H^{\ddagger}$ = 4.9 (±0.2) kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −6.3 (±2) cal mol^{-1} deg^{-1} were obtained. These quantities imply a considerable rotational barrier for inversion of the *tert*-butyl substituents of the bridging thiolate ligands.

Structure Descriptions. The X-ray analyses have shown that **1** and **2** correspond to two conformational isomers of the title complex. Crystals of **1** are built up from discrete molecules of the anti isomer of the complex and diphenylacetylene, for the shortest intermolecular contacts between complex and acetylene are 3.62 (5) Å between Br and C(33) at $(1 + x, y - 1, 1 + z)$. Similarly, the shortest distance between complex molecules is 3.66 (4) Å between C(7) and C(26) at $(x, y, 1 + z)$. Crystals of **2** contain discrete molecules of the syn isomer of the complex. The shortest intermolecular distance of approach is 3.63 (2) Å between Br and C(6) at $(x, y, 1 + z)$. The syn isomer has crystallographic symmetry imposed since it lies on a mirror plane at y = 0.25. There is close agreement in bond distances between **1** and **2** and good agreement internally in each structure between chemically equivalent bond distances. Only bond angles vary noticeably; some but not all such variations can be explained on the basis of steric repulsions due to the bulky *tert*-butyl groups on the bridging thiolato ligands.

In discussing the structures, it is convenient to view **1** and **2** as adducts between the formally Mo(II) d^4 complex, *cis*-Mo(*t*-BuS)$_2$(*t*-BuNC)$_4$ (**3**),[7] and a Cu(I) d^{10} fragment, CuBr. Some weighted least-squares planes are given in Table V.[13] The MoS_2Cu entity is significantly buckled in both **1** and **2** with short Mo---Cu distances of 2.628 (2) and 2.615 (2) Å, respectively. Each Mo atom has a distorted octahedral geometry, with indistinguishable Mo–S distances ranging from 2.409 (2) in **2** to 2.415 (3) Å in

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Table VII. IR and ^{1}H NMR Spectra

IR Spectra (cm^{-1}) of Nujol Mulled 1 and 2

compd	ν(N≡C)	δ(*t*-Bu)	other bands	
1	2125	1230	762	536
	2090 (sh)	1200	727	513
	2070	1160	719	421
	2010		693	
2	2140	1230	727	500
	2063	1200	719	451
	2030	1155	693	421
	1960		546	399
			530	

^{1}H NMR of 2 in Chlorobenzene at 27 °C[a]

δ, ppm	rel intensity	assignment[b]
1.786	2	*t*-BuS(syn)
1.721	3	*t*-BuS(anti)
1.288	2	equatorial *t*-BuNC(syn)
1.241	3	equatorial *t*-BuNC(anti)
1.179	1	axial *t*-BuNC(syn)
1.008	3	axial *t*-BuNC(anti)
0.969	1	axial *t*-BuNC(syn)

[a] The spectral data of **1** were essentially identical with those of **2** shown here. See Figure 5 for the spectra at temperatures 69 (coalesce temperature) and 110 °C. [b] The assignment was made as follows; the three signals due to axial *t*-BuNC can readily be assigned on the basis of their relative intensities. Note two signals for the syn isomer. This gives the 2:3 isomer ratio. Then the equatorial *t*-BuNC signals can readily be assigned from their intensities.

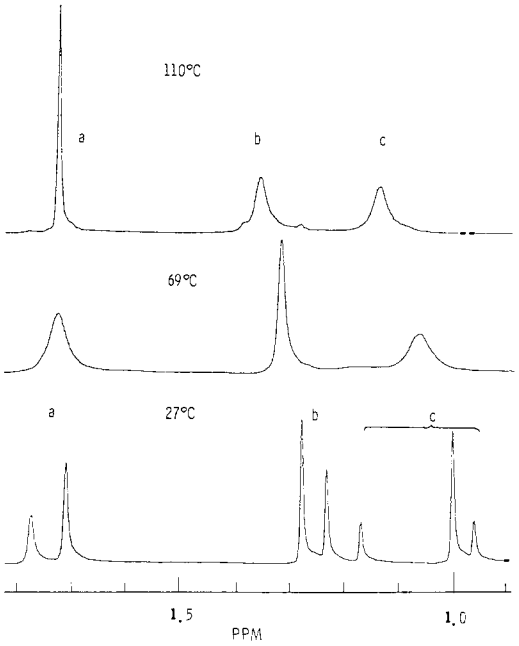


Figure 5. Temperature-variant ^{1}H NMR spectra of a chlorobenzene solution of complex **2**: (a) $(CH_3)_3CS$, (b) equatorial $(CH_3)_3CNC$, (c) axial $(CH_3)_3CNC$.

1, close to those of 2.372 (3) and 2.374 (3) Å found in **3**. In forming the MoS_2Cu fragment, the S–Mo–S angles of 105.0 (1) in **1** and 105.1 (1)° in **2** are much smaller than that of 115.3 (1)° in **3**. As chelation to CuBr narrows the S–Mo–S angle, so the C–Mo–C angle opposite increases from 73.7 (4) in **3** to 76.4 (5) in **1** and 79.6 (3)° in **2**, values still significantly different from ideal octahedral geometry. The axial isocyanide ligands are not perpendicular to the MoS_2Cu planes but instead bend significantly away from the bulky *tert*-butyl substituents upon the bridging thiolato ligands. This is clearly shown by the nonbonding intramolecular interactions listed in Table VI;[13] in the anti-upright isomer **1**, S---C(4) distances are 3.01 (1) and 3.49 (1) Å, and S---C(1) distances are 2.93 (1) and 3.53 (1) Å, whereas in the syn-upright species, S---C(4) are equal (due to *m* symmetry) at 3.11 (1), as are S---C(1) at 3.41 (1) Å, the longer distance being on the same side of the MoS_2Cu plane as the *t*-Bu groups.

The Cu atoms have almost exact trigonal-planar coordination geometry: in **1** within experimental error, in **2** the Cu atom is displaced by 0.026 (2) Å from the SSBr plane (Table V).[13] The Cu–Br distances are equivalent, 2.317 (2) Å in **1** and 2.314 (2) Å in **2**, as are the Cu–S distances of 2.234 (3) and 2.244 (3) Å in **1**, and 2.233 (3) Å in **2**. Comparable Cu–S distances averaging 2.259 (6) Å were found in the trigonal $Cu(SPMe_3)_3ClO_4$ complex,[16] in which the angles at Cu ranged from 118.2 (2) to 122.6 (2)°. In **1** they vary from 117.5 (1) to 122.4 (1)° and in **2** from 117.8 (1) to 121.1 (1)°. Three coordinate Cu atoms were also found in *cyclo*-tri-(μ-(trimethylphosphine sulfide))tris(trichlorocopper(I)),[17] in which trigonal coordination to bridging S atoms and a terminal Cl ligand was seen (Cu–Cl 2.209 (2) and 2.220 (1) Å; Cu–S 2.264 (1), 2.265 (1), and 2.267 (2) Å; angles varying from 109.8 (1) to 125.2 (1)°).

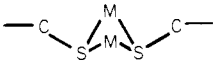
The bridging S atoms have distorted geometries, with angles varying from 68 to 121°. The Mo–S–C angles are significantly larger than the Cu–S–C angles. The values observed for Mo–S–C in **1** are 121.8 (6) and 120.8 (4)°, and 120.4 (3)° in **2**, only slightly larger than those of 119.2 (4) and 119.7 (4)° in **3**. Whereas the S---S nonbonding distance was 4.010 (3) Å in **3**, it is 3.824 (3) Å in **2** and 3.841 (4) Å in **1**, all greater than the sum of the van der Waals radii, 3.60 Å (Table VI).[13] The Mo–S–Cu angles of 68.6 (1) and 68.8 (1)° in **1** and 68.4 (1)° in **2** are even smaller than the value of 74° found in $Mo_2(\mu\text{-}t\text{-BuS})_2(CO)_8$,[6] formally Mo(I) where the Mo---Mo distance is 2.294 Å.

As was observed in complex **3**, the isocyanide ligands show considerable deviations from linearity. In **1**, angles at the coordinated C atom vary from 171 (1) to 177 (1)°, in **2** from 170 (1) to 179.5 (8)°, and in **3** from 172.8 (8) to 179.0 (8)°. Similarly, the angles at the N atom vary from 165 (1) to 197 (1)° in **1**, from 156 (1) to 173 (1)° in **2**, and from 160 (1) to 172 (1)° in **3**. In **2** and **3**, which each contain cis thiolato ligands with syn *tert*-butyl groups, the greatest deviation from the expected linearity is such as to bend the *tert*-butyl group *away* from the sp^2 lone pair on the μ-S atoms (Figure 2). The S(1)---C(4) and S(1)---N(4) nonbonded distances are 3.11 (1) and 4.03 (1) Å, respectively, however. A lesser distortion of 165 (1)° was observed in **1**, where the thiolato substituents adopt an anti arrangement. Although the implication is that an increase in sp^2 character is occurring at N(2) and N(4) in **3**, and at N(4) in **2**, this is still less than the mean values of 130 (2)° for the axial (compared to 170 (3)° for the equatorial) isocyanide ligands in $[Ru(t\text{-BuNC})_4PPh_3]$.[18] Compared to the low IR ν(N≡C) frequency of 1830 cm^{-1} in the Ru complex, which reflects the bent isocyanide ligands, the IR bands of **1** (2125–2010 cm^{-1}) and **2** (2130–1960 cm^{-1}, see Table VII) are not particularly low. Compared to the ν(N≡C) frequencies of the parent **3** (2120–1997 cm^{-1}), however, the bands of **2** shift considerably to the lower frequency region. This is consistent with the trend in CNC angles of the isocyanide ligands in **1** and **2** (Table IV).

Discussion

A survey of the recent literature for bimetallic clusters showed us that there are a number of dinuclear complexes formed by d^4–d^4 or d^{10}–d^{10} metals, either with or without bridging ligands. There is, however, to the best of our knowledge, no example of a d^4–d^{10} compound. As the present MoCu complexes have two thiolate bridges, the metal formal oxidation states could be regarded as either Mo^I–Cu^{II} (d^5–d^9) or Mo^{II}–Cu^I (d^4–d^{10}). The latter formulation is more appropriate in view of the IR isocyanide stretching vibrations (see Table VII) and the structural parameters (Table IV), which are comparable to those found in the molybdenum(II) compound **3**. In fact, the Mo atom in compound **2** retains the overall geometry of **3** apart from a change in the SMoS angle (vide infra). The Mo(II) moiety in **2** can therefore be regarded as a bidentate ligand to the Cu(I) center, through bridging thiolato groups. In a similar fashion, the Mo(VI) thioanion MoS_4^{2-} acts as a bidentate ligand and forms a wide range of multimetal complexes.[4] The MoCu complexes **1** and **2** are diamagnetic and, in contrast to the parent compound **3**,[19] relatively inert to substitution with nucleophiles such as acetylenes. In fact, no reaction took place between **3** and PhC≡CPh in boiling acetone. Interestingly, however, the conformation of the syn-upright 2-propanethiolate bridges of **2** changed into the anti-upright one as seen in **1**.

The $M_2(\mu\text{-SR})_2$ core of the various known bis(thiolate)-bridged dinuclear compounds shows interesting variations depending on the metal atoms. For example, the Fe_2S_2 core of $Fe_2(\mu\text{-EtS})_2(CO)_6$[20] forms a bent four-membered ring (**5**), whereas the core



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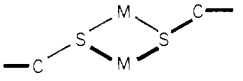

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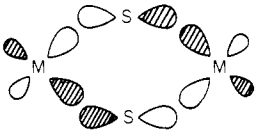
of so-called Roussin's red ethyl ester, $Fe_2(\mu\text{-EtS})_2(NO)_4$, is exactly planar (**6**).[21] In both **5** and **6**, the two CS vectors lie in the symmetry plane bisecting the MSM angle. The $MoCu(SR)_2$ core of **1** assumes roughly the configuration **6**, which may be called anti-upright. However, there is a subtle difference in that the CS vectors of **1** (and also **2**) are not contained in the (pseudo) symmetry plane containing the two S atoms. In the case of **5** and **6**, the lone-pair orbital of each sulfur atom is shared equally by the two metal atoms (**7**). This is not so for compounds **1** and



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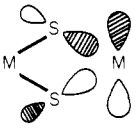

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2. The normals to the planes formed by MoS(1)C(21) and MoS(2)C(25) define the directions of the S 3p lone-pair orbitals. These normals made angles of 4 and 6° in **3** with the MoSS plane. Coordination of the CuBr fragment results in comparable values of 9.1 (7) and 6.6 (5)° in **1** and 10.9 (4)° in **2** with the MoSSCu plane. By comparison, the CuS(1)C(21) and CuS(2)C(25) planes in **1** make angles of 59.5 (6) and 65.8 (4)° with the CuS(1)S(2) plane, whereas in **2** the value found is 59.6 (4)°. A value of 60° between these planes and angles of zero made by the normals to the MoSC planes with the MoSS plane would require that the S 3p lone-pair orbitals lie exactly in the MoS_2Cu plane. In both **1** and **2** this is almost the case. This core geometry indicates that the sulfur p lone-pair orbitals are directed toward the Cu(I) center, as in **8**. The molybdenum thiolato fragment is acting as a donor and the CuBr fragment as an electron-accepting center presumably with its 4p orbital. A question then arises. Is there a net charge

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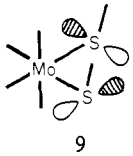
transfer from Mo(II) to Cu(I)? An answer may be obtained from the IR NC stretching frequencies and the molecular parameters of the Mo(t-BuS)$_2$(t-BuNC)$_4$ fragment. The highest ν(NC) of **1** or **2** is a little higher than that of **3**, but the lowest ν(NC) of **2** is somewhat lower than that of **3**. These data therefore are best regarded as being comparable. This is understandable. The Mo–Cu distance is less than the sum (2.80 Å) of the atomic radii[22] of molybdenum and copper, so the electron transferred to the copper atom could well be returned to the molybdenum through metal–metal interactions. In short, the MoS_2Cu core should be regarded as a delocalized system.

Let us take a close look at the structural details to examine the effect of the CuBr moiety upon the known molecule *cis*-Mo(t-BuS)$_2$(t-BuNC)$_4$ (**3**). A series of molecular orbital calculations has been described for the simplified molecule *cis*-Mo(SH)$_2$(CNH)$_4$, assuming a low-spin d^4 electron configuration at the Mo atom, dominant π-acceptor characteristics for the isocyanide ligands, and donor properties for the thiolate ligands.[7] The potential surface calculation showed clearly that the ideal octahedral geometry was not the most stable in thermodynamic terms. In "a rather soft surface" a potential minimum was found near S–Mo–S = 102.5° and C–Mo–C = 80.0° in the equatorial plane. In view of the approximate nature of the EHMO calculation, the small discrepancies between these calculated values and those of 115.3 (1) and 73.7 (4)° found in **3** are acceptable. The larger S–Mo–S angle observed for **3** could arise from a repulsive interaction of the two *tert*-butyl groups of t-BuS ligands, since the calculation is based on the hypothetical molecule Mo(HS)$_2$(CNH)$_4$. Such a steric repulsion will be relieved in the isomer of anti conformation. The present X-ray data enable us to examine the importance of steric effects in the dinuclear complex. As described, the S–Mo–S angles found in the anti (**1**) and the syn conformer (**2**) are identical (105°) within experimental error, a feature indicative of an insignificant contribution from steric factors to the Mo coordination geometry in **1** and **2**.

The decrease in S–Mo–S angle in **1** and **2**, compared to **3**, should then be ascribed to an electronic factor. The S–Mo–S and C–Mo–C values for **1** and **2** each give points that lie in the area between the –0.20-eV contour and the –0.24-eV minimum (Figure 6 of ref 7), implying that a very small energy assistance is necessary to achieve the angles. The assistance is apparently secured by the interaction **8**. The highest occupied MO(homo) of **3** are metal d$_{yz}$ and d$_{xz}$, and below the homo there is a MO comprised almost entirely of an out-of-phase combination of the S lone-pair orbitals (**9**) lying in the equatorial plane, an interaction primarily re-



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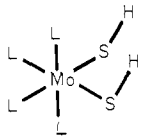
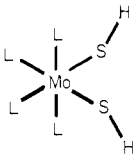
sponsible for the wide S–Mo–S angle in **3**. The filled orbital **9** will be stabilized through **8**, leading to the smaller S–Mo–S angle in **1** or **2**.

The total energies of conformational isomers syn- (**10**) and anti-upright (**11**) were calculated previously. Their values were almost comparable, **11** being slightly more stable, but only by 0.007 kcal mol^{-1}. Although the relative energies of isomers **1** and



10 (L = CNH)



11 (L = CNH)

2 have not been calculated, their thermodynamic stabilities may be deduced to be comparable on the basis of the relative molar ratio (2:3) in the solution of **2** as assessed by the relative intensities of ^{1}H signals. The small energy difference is borne out by our fortuitous crystallization of the anti-upright isomer **1**, in the presence of diphenylacetylene, from an acetone or acetone–toluene mixture, whereas the syn-upright isomer **2** was obtained in the absence of the acetylene. We also attempted to convert **2** into the anti isomer **1** by recrystallization from toluene in the absence of diphenylacetylene; an amorphous mixture of both isomers was obtained. Thus the presence of the acetylene molecule is necessary to form a pure crystalline sample of the anti isomer.

The energy barrier to interconversion around the Mo–S bond was calculated by EHMO to be 6.4 kcal mol^{-1} for the hypothetical molecule, *cis*-Mo(SH)$_2$(CNH)$_4$.[7] With the bulky *tert*-butyl groups, the value for **3** can undoubtedly be greater. The ^{1}H as well as ^{13}C NMR spectra of **3**, however, indicated a rapid equilibration between syn and anti conformations as low as –100 °C, suggesting an even lower energy barrier. In contrast, the ^{1}H NMR spectrum of **2** shows clearly the presence of two conformers even at room temperature, and the experimental kinetic barrier for the interconversion is about 7 kcal mol^{-1}. The higher barrier than that for **3** is obviously due to the four-membered ring MoS_2Cu, where the endo rotation need not be considered.

Finally it should be noted that the present synthesis of molybdenum-containing mixed-metal compounds is not limited to the compounds **1** and **2**. For example, on adding "Pd(t-BuNC)$_2$" to Mo(t-BuS)$_2$(t-BuNC)$_4$, a mixed bimetal compound, MoPd(μ-t-BuS)$_2$(t-BuNC)$_5$, was obtained, as will be described elsewhere. The molecular structure involves a planar three coordinate Pd(0) fragment and is quite analogous to the anti-upright **2**.

In conclusion, these syntheses based on the cis bis(thiolato)-molybdenum fragment are applicable to the preparation of a variety of mixed d^4–d^{10} metal clusters, and further studies are underway. Although the synthesis of the title compound is carried out under rigorously dry, anaerobic conditions, we have demonstrated that a relatively air- and moisture-stable MoS_2Cu fragment can be formed that contains bridging thiolato ligands. This is significant, for the disorders experienced by ruminants pastured on soils rich in Mo have been traced to a deficiency of Cu,[3] and a number of complexes have been prepared by using thiomolybdate in MoS_4^{2-} as models for the strong complexation of Cu in tissue in the form of [Cu]MoS_4^{2-}–protein complexes.[4] The present work suggests that a more diverse range of Mo–S–Cu interactions should be considered.

Registry No. 1, 83418-26-2; **2**, 83946-17-2; Mo(t-BuS)$_4$, 74656-39-6; CuBr(t-BuNC)$_3$, 15680-86-1.

Supplementary Material Available: Structure amplitudes for isomers **1** and **2** and tables of the thermal parameters for **1** and **2**, the least-squares planes, and the nonbonded interactions (22 pages). Ordering information is given on any current masthead page.

(22) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199–3204.