Table I. Products and Yields of the Photoreaction of 1 and 2 in Various Polychloromethanes[a]

	products from 1			products from 2		
solvent	conv, %	3, %	13, %	conv, %	6, %	14, %
CCl_4[b]	85	0	86	85	0	80
$CDCl_3$	67	49	32	78	0	66
CH_2Cl_2	57	63	0	27[c]	37	41

[a] Unless otherwise noted, irradiation was carried out for 1 h with a 450-W high-pressure Hg arc lamp filtered by Pyrex glass. The yields were determined by ^1H NMR. [b] Hexachloroethane was produced in 60% and 53% yields for the reactions of 1 and 2, respectively. [c] After irradiation for 8 h.

A similar mechanism may be applied to the photoreaction of **2**. Relatively slow disappearance of **2** is in good accord with the known low reactivity of germyl radicals toward aromatic substitution.[12,13]

Intermediacy of diradicals **8** and **9** in the reaction was supported by the photoreaction in various polychloromethanes in which dichlorination took place competitively with the extrusion of the divalent species to afford 2,2′-bis(chlorodimethylsilyl)biphenyl (**13**) and the germanium analogue (**14**)[14] from **1** and **2**, respectively (path b in Scheme I). The results are summarized in Table I. In carbon tetrachloride, extrusion of the divalent species from **8** and **9** was completely suppressed and the dichlorinated compounds were obtained in high yields. The relative importance of the latter products decreased in the order $CCl_4 > CDCl_3 > CH_2Cl_2$, in accord with the reported relative rates of chlorine abstraction of silyl radicals.[15]

Contrary to the photolysis of dodecamethylsilacyclohexane at 77 K,[16] **1** was not photolyzed at temperatures lower than 200 K. Instead, irradiation of **1** at 77 K in a 3-methylpentane glass matrix with a 500-W xenon lamp afforded a triplet species which was detected by ESR and emission spectra (D = 0.0988 and E = 0.0040 cm^{-1}, $E_T \simeq 64$ kcal mol^{-1}, $\tau_T < 1$ s). These facts suggest that the intramolecular ipso substitution requires a small but significant activation energy. Since the photoreaction of **1** was neither sensitized by benzophenone triplet (E_T = 68.6 kcal mol^{-1})[17] nor quenched by piperylene ($E_T \simeq 59$ kcal mol^{-1}), the excited state responsible for the photoreaction of **1** should be the lowest excited singlet state.

Registry No. 1, 85590-07-4; **2**, 87842-16-8; **3**, 13688-68-1; **4**, 38041-07-5; **5**, 55644-09-2; **6**, 64526-49-4; **7**, 5764-66-9; **12**, 87842-17-9; **13**, 87842-18-0; **14**, 87842-19-1; dimethylmethylsilane, 760-32-7; 2,3-dimethyl-2-butene, 563-79-1; 2,3-dimethylbuta-1,3-diene, 513-81-5; dimethylsilylene, 6376-86-9; dimethylgermylene, 74963-95-4; di-*tert*-butyl peroxide, 110-05-4; 2,2′-dilithiobiphenyl, 16291-32-0; 1,2-difluoro-1,1,2,2-tetramethyldisilane, 661-68-7.

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(14) **13**: ^1H NMR (CCl_4) δ 0.26 (s, 6H), 0.35 (s, 6 H), 7.15–7.95 (m, 8 H); MS, m/e 338 (M^+, 1.3), 195 (100), 93 (26); high-resolution mass spectrum, m/e 338.0461 (calcd for $C_{16}H_{20}Si_2{}^{35}Cl_2$, 338.0481). **14**: ^1H NMR (CCl_4) δ 0.37 (s, 6 H), 0.67 (s, 6 H), 7.15–8.00 (m, 8 H); MS, m/e (%) 413 (M^+ − 15, 22), 243 (100), 152 (84), 139 (88). Hydrolysis of **13** and **14** afforded the corresponding siloxane and germoxane, respectively, in quantitative yield.

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A Novel Molybdenum–Iron Thiolato Complex: $MoFe_2(\mu\text{-}t\text{-}BuS)_4(CO)_8$

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As part of our continuing interest in developing a novel molybdenum thiolato chemistry based on the versatile Mo(IV) complex $Mo(t\text{-}BuS)_4$,[2] we have studied possible formation of Mo–Fe mixed-metal compounds therefrom. In this communication we wish to report preparation, spectroscopic properties, and molecular structure of the title compound, which possesses a quite unusual coordination environment arund the Mo atom.

A mixture of $Mo(t\text{-}BuS)_4$ (0.4 mmol) and $Fe_2(CO)_9$ (1.2 mmol) dissolved in toluene was heated under a nitrogen atmosphere (65 °C, 24 h) to give a dark brown reaction mixture. Volatile materials being removed in vacuo, the resulting residue was washed with a small amount of hexane. The residue was then redissolved in toluene and the solution was chromatographed on alumina column (toluene eluent) to isolate a solid which after recrystallization from toluene gave dark brown crystals of composition $MoFe_2(t\text{-}BuS)_4(CO)_8$ (**1**), mp 175 °C dec. The yield amounts to 45% based on $Mo(t\text{-}BuS)_4$, the other product identified being only a small amount of the red diiron compound $Fe_2(\mu\text{-}t\text{-}BuS)_2(CO)_6$,[3] mp 75 °C (IR ν(CO) 2065, 2030, 1995, 1987; mass spectrum, m/e 458). The reaction employing a lower $Fe_2(CO)_9$:$Mo(t\text{-}BuS)_4$ ratio, e.g., 1:1, gave a similar result but with a lower yield of **1** (<15%).

Formulation of **1** was established by elemental analysis[4] and mass and other spectroscopic data. Thus, the mass spectrum[5] showed the parent ion (m/e 790) of fairly strong intensity accompanied by six isotopic bands (m/e 784, 786, 787, 788, 789, and 792) reflecting the isotopic distributions of Mo and Fe atoms. The fragmentation occurs loosing successively the eight carbonyl ligands and four t-Bu groups resulting in the strongest bands centered at m/e 338 and accompanied by 13 weaker peaks, which are readily assigned to a fragment ion $MoFe_2S_4{}^+$. The IR CO stretching bands occur at 2058, 2040, 1997, 1989, 1980, 1908, and 1864 cm^{-1}. The two low-frequency bands, 1908 and 1864 cm^{-1}, may be ascribed to the two carbonyl ligands attached to the Mo atom on the basis of the bent geometry (vide infra). The ^1H NMR spectrum (in toluene-d_8) measured at 27 °C shows two t-Bu proton signals at δ 1.31 and 1.38. The two singlet signals coalesce at ~70 °C and become a sharp single signal at higher

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(5) Recorded on the JEOL OISG-2 mass spectrometer (ionizing potential and current are 75 eV and 200 μA, respectively; sample temperature, 150 °C).

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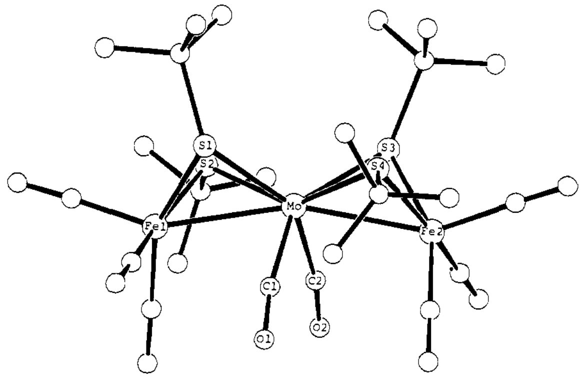

Figure 1. Molecular structure of MoFe$_2$(μ-*t*-BuS)$_4$(CO)$_8$, a view perpendicular to the C$_2$ axis. Important bond distances are as follows: Mo–Fe1 2.754, Mo–Fe2 2.759, Mo–S1 2.517, Mo–S2 2.448, Mo–S3 2.537, Mo–S4 2.441, Fe1–S1 2.294, Fe–S2 2.266, Fe–S3 2.293, and Fe2–S4 2.268 Å, esd's are 0.001 Å for these distances. The nonbonded S1···S2 and S3···S4 distances are 2.961 (2) and 2.989 (2) Å, respectively.

temperature (δ 1.38 at 110 °C), indicating equilibration of two *t*-Bu substituents of the bridging *t*-BuS groups. The temperature variant behavior is reversible. The spectrum was also examined in toluene-d_8 with added *t*-BuSLi (**1**:*t*-BuS$^-$ = 1:1). The two singlets due to **1** coalesce at the same temperature (~70 °C) without affecting the signal due to *t*-BuS$^-$ (δ 1.19), a result implying an intramolecular site-exchange mechanism. A similar conformational equilibration was reported for syn and anti configurations of *t*-BuS bridged dinuclear complex (*t*-BuS)$_4$Mo(μ-*t*-BuS)$_2$CuBr.[2e] The ^{13}C signals for both methyl carbon and tertiary-carbon atoms of *t*-Bu groups also split into two at room temperature (δ (Me$_4$Si) 34.36 and 35.77 for (CH$_3$)$_3$C; 48.48 and 53.28 for (CH$_3$)$_3$$C$). The signals for CO ligands are not observed.

The molecular structure of **1** was determined by X-ray crystallography.[6] The molecule possesses a noncrystallographic C$_2$ axis passing through the Mo atom and approximately bisecting the C1MoC2 angle (77.0°) (Figure 1). Selected structural parameters are also indicated in Figure 1. The Fe1-Mo-Fe2 angle is 160.43 (3)° and the dihedral angle between Mo–S1–S2 and Mo–S3–S4 is 120.89 (4)°. This molecular framework may remind one of chiroptera or bat. The Mo coordination geometry cannot be described in terms of simple symmetry. At the best the geometry (neglecting the Fe atoms) may be approximated as a highly distorted and flattened trigonal prism. This open structure can be rationalized in terms of the formal electron count (Lauher rule[7]). Electron-precise trinuclear carbonyl cluster M$_3$(CO)$_{12}$ has 48 cluster valence electrons (CVE), whereas **1** has 50 CVE regarding each *t*-BuS group as a four-electron donor.

The Mo–Fe distances (2.754 (1) and 2.759 (1) Å) are somewhat longer than those in triply thiolate bridged Mo–Fe bonds (2.559 and 2.309 Å) in the double cubane cluster (Et$_4$N)$_3$[Mo$_2$Fe$_7$S$_8$(SEt)$_{12}$],[8] reflecting the lower oxidation states of the metal ions in **1**. There are two distinct Mo–S distances, one pair (Mo–S2 and –S4) is short and the other (Mo–S1 and –S3) long (Figure 1).[9] Another salient feature in the structure is the coordination geometry of CO ligands on the Mo atom. The reason for the bent CO coordination (169.5 (4) and 170.8 (4)°) may be ascribed to the interaction with the Fe atoms (C1–Fe1 = 2.734 (5) vs. C1–Fe2 = 3.499 (5) Å and C2–Fe2 = 2.810 (5) vs. C2–Fe1 = 3.580 (5) Å). The CO ligands may then be classified as a semibridging CO, and the low stretching frequencies are consistent with this view.

Despite the open structure, the molecule shows remarkable thermal stability as manifested in its mass spectrum and solution NMR data described above. This Mo–Fe thiolato compound adds an example of a novel structure to the Fe–Mo cofactor model chemistry of current interest.

Acknowledgment. K.H. and T.H. are indebted to the Crystallographic Research Center, Institute for Protein Research, Osaka University, and Computation Center Osaka University, for computer calculations.

Registry No. 1, 87803-90-5; Mo(*t*-BuS)$_4$, 74656-39-6; Fe$_2$(CO)$_9$, 15321-51-4.

Supplementary Material Available: Tables of structural amplitudes, atomic coordinates, thermal parameters, bond lengths, and bond angles and structural figure (15 pages). Ordering information is given on current masthead page.

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(6) Single crystals grown from toluene are monoclinic, space group $P2_1/n$ with a = 21.694 (6) Å, b = 15.828 (4) Å, c = 9.892 (2) Å, β = 94.53 (2)°, and Z = 4 (d_{calcd} = 1.546 g cm^{-3}); μ(Mo Kα) = 15.01 cm^{-1}. Three-dimensional X-ray diffraction data were collected for 5950 independent reflections on a Philips PW1100 automatic four-circle diffractometer with graphite-monochromatized Mo radiation. The structure was solved by using the heavy-atom technique for 4460 reflections having $I > 3\sigma(I)$ and $2\theta < 50°$. Structural parameters have been refined to convergence [R(unweighted, based on F) = 0.038] in cycles of weighted cascade-blocked least-squares refinement that employed anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. See also supplementary material.

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^{15}N Spin Exchange in a Protein

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The observation of through-space interactions among nuclear spins provides a general method for molecular structure determination. These interactions are most conveniently observed with two-dimensional homonuclear spin-exchange experiments.[1] The best known of these is the NOESY sequence used in high-field ^{1}H NMR on molecules as complex as proteins and nucleic acid in solution.[2] Recently, related methods have been found to detect through-space dipolar interactions among ^{13}C sites in the solid state.[3-5] The acquisition of data concerning spin interactions over reasonably long molecular distances is an important new capability in NMR spectroscopy.

We have adapted the solid-state dilute-spin-exchange experiments described by Maciel[3,4] and Ernst[5] for ^{15}N NMR of biopolymers. High levels of ^{15}N enrichment increase the probabilities for through-space spin interactions via homonuclear dipolar couplings among nearby sites. In order to observe off-diagonal cross peaks, the sites must be in close proximity and have resolved resonances. In the previous solid-state spin-exchange experiments, magic-angle sample spinning[3,4] and molecular reorientation[5] resulted in isotropic chemical shift spectra where resolution was based on different chemical environments. Here magnetic

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