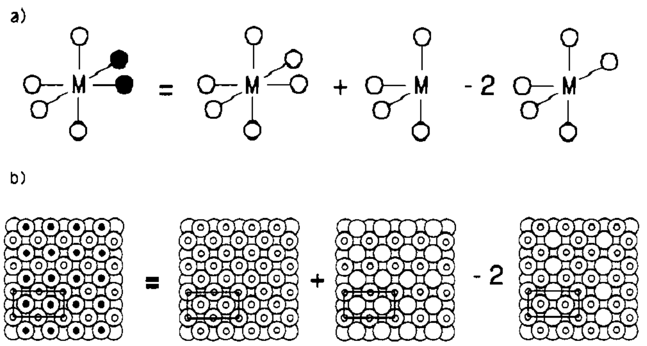

Figure 2. Definition of the pair potential used in Figure 1 in symbols.

of the individual bond energies of the two atoms or fragments and the total bond energy when the two fragments are coordinated at the same time. For an ML_6 species it is simply the energy(ML_6) + energy(ML_4) − 2 × energy(ML_5). Positive and negative pair potentials represent respectively a repulsion and attraction between the two fragments. For the systems we will discuss here, the pair potential will thus be directly calculated rather than coming from some empirical model. Although the bond energy from such calculations is not reliable, the pair potential obtained via this isodesmic (same number of linkages) process should be well approximated.

Figure 1 shows the pair potential calculated (using the extended Hückel model[5]) between two L groups in several geometries, as a function of central atom or bulk atom electron count (L for our purposes is a hydrogen atom, but similar results are found for other ligands). In all cases of Figure 1 the pair potential is calculated between the shaded ligands as described in Figure 2 for the O_h ML_6 complex and the (100) surface of a fcc metal.

Notice the two large peaks in the plot of Figure 1a that represent the pair potential in an octahedral transition-metal complex ML_6. The first rises steeply past six electrons and the second past ten electrons. The amplitude of these peaks are very large, larger indeed than the metal–ligand bond energy. Thus for the hypothetical species (d^8) $Fe(CO)_6$ the pair potential is so repulsive that one of the CO groups is ejected to give $Fe(CO)_5$. A 20-electron molecule is thus converted into an 18-electron one by ligand loss. For (d^6) $Cr(CO)_6$ the pair potential is negligibly small and no ligand is ejected. $Fe(CO)_5$ and $Cr(CO)_6$ are both stable molecules. The foot of the second peak of Figure 1a occurs at the filled d shell. A molecule with this electronic configuration is SF_6 (SeF_6), a stable octahedral species. With two extra electrons, the pair potential is repulsive and the hypothetical molecule IF_6^- loses a ligand to give stable square pyramidal IF_5.[6]

Similar considerations apply to the pair potential (Figures 1b,c) calculated for two L atoms in the molecules M_2L_{10} and M_3L_{12}. The d electronic configuration corresponding to the foot of the first peak is d^7 and d^8 per metal atom respectively, appropriate for the stable isoelectronic molecules $Mn_2(CO)_{10}$ and $Fe_3(CO)_{12}$. The electronic configuration at the foot of the second peak in Figure 1b is for an atom with a filled d-shell, plus a pair of central atom s/p electrons per molecule, an electron count appropriate for the species S_2F_{10}. The extra pair of electrons is associated with the S–S bond. For M_3L_{12} the foot of the large peak at 12 electrons corresponds to the filling of all three M–M bonding orbitals. The small peak at 11.33 electrons represents the Jahn–Teller instability associated with the half-filling of the e′ orbitals of this set. The result we get from here is that the pair potential is small as long as we do not put the $(n + 1)$th pair in an orbital which is separated by a large gap from that holding the nth pair or half-fill degenerate levels. This represents therefore the rule that stable geometries occur in general with large HOMO–LUMO gaps.

In all of these molecular examples, the location of the peaks in a plot of pair potential versus electron count delineate those areas where traditional electron-counting considerations predict that species with the given stoichiometry are unlikely to exist. Elsewhere, we describe[7] other aspects of this new molecular parameter. Another set of calculations for the square-planar geometry shows stability for 16 electrons; one for a B_6H_6 cluster, stability for seven skeletal electron pairs. Molecules with less than the magic number of electrons are expected to be stable *with respect to ligand loss*. Thus both (d^6) $Cr(CO)_6$ and (d^5) $V(CO)_6$ are known. The pair potential arguments make no statement as to stability with respect to ligand gain for these molecules.

As the number of metal atoms increases the foot of the d-region peak moves to a higher electron count, d^6 for ML_6, d^7 for M_2L_{10}, and d^8 for M_3L_{12}. Also the amplitude of the potential decreases with the number of metal atoms.

The form of the pair potential plot for two L atoms adsorbed on a (100) surface of a fcc metal (Figures 1d and 2b) is then readily appreciated. The foot of the peak in the pair potential has moved to around $d^{9.2}$ and its amplitude is now below the metal–ligand bond energy. The result for the hypothetical pattern chosen here (Figure 2) tells us that there are no repulsive forces between second nearest neighbors within a 1 × 1 pattern of a fcc metal (100) surface up to d^{10} but that repulsion occurs after d^{10}. Thus the surface analogue of the *molecular* effective atomic number rule controls the magnitude of the adatom–adatom pair potentials that set the form of the adsorption patterns and phase diagram for adsorption. There is no fierce electronic destabilization of a surface structure that contains "too many" adsorbed L units as there is in molecules, although the usual steric constraints will apply.

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(5) For all calculations, the extended Hückel method was used. For the molecular case, the usual Cr parameters and for the tight-binding computatation of a five-layer slab of a fcc metal (both sides covered with hydrogen atoms in on-top position) the usual Ni–metal parameters were used. All M–H and M–M distances were fixed to 1.8 and 2.49 Å, respectively.

(6) With two extra electrons, XeF_6, though stable as a six-coordinate molecule, is not octahedral.

(7) Burdett, J. K.; Fässler, T. F. Submitted for publication.

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d,l- and *meso*-Bis(α-mercaptobenzyl)dimethylsilane: New Hindered Bidentate Ligands and a Novel Binuclear Molybdenum Complex Formed Therefrom

Silicon has been shown to be a useful structural element in thiolate ligands by allowing regulation of steric hindrance and solubility in complexes involving silylated methanethiols,[1] benzenethiols,[2] and pyridine-2-thiols[3] and by functioning as a con-

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(1) Block, E.; Aslam, M. *Tetrahedron Lett.* **1985**, *26*, 2259. Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Siegel, G. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1674. Block, E.; Aslam, M. *J. Am. Chem. Soc.* **1985**, *107*, 6729. Tank, K.; Aslam, M.; Block, E.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 488. Koo, B.-K.; Block, E.; Liu, S.; Zubieta, J. *Polyhedron* **1988**, *7*, 1397.

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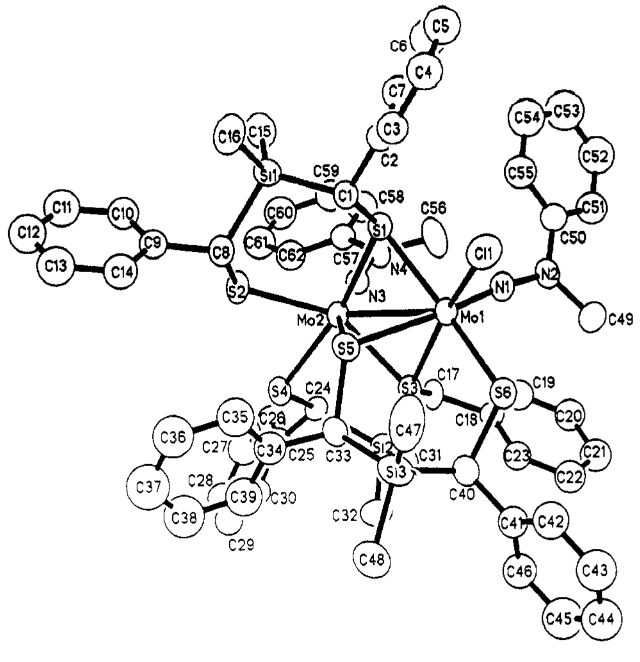


Figure 1. ORTEP view of the structure of the anion of **4**, showing the atom-labeling scheme.

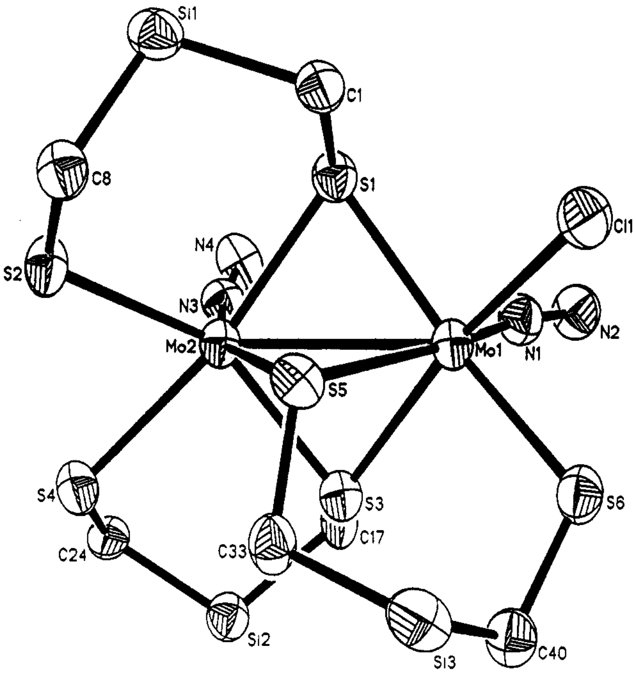
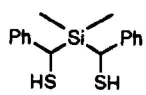


Figure 2. Perspective view of the anion of **4**, with methyl and phenyl groups omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–Mo2, 2.900 (1); Mo1–Cl1, 2.476 (3); Mo1–S1, 2.460 (3); Mo1–S3, 2.429 (2); Mo1–S5, 2.594 (2); Mo1–S6, 2.450 (4); Mo1–N1, 1.748 (9); Mo(2)–S1, 2.459 (2); Mo2–S2, 2.430 (2); Mo1–S3, 2.411 (3); Mo2–S4, 2.505 (2); Mo2–S5, 2.558 (3); Mo2–N3, 1.768 (10); N1–N2, 1.329 (11); N3–N4, 1.326 (15); N1–Mo1–S5, 167.0 (3); N3–Mo2–S5, 157.4 (2); Mo1–N1–N2, 171.7 (10); Mo2–N3–N4, 168.4 (6).

nector in the synthesis of dithiols, e.g. bis(mercaptomethyl)dimethylsilane[1] and bis(2-mercaptophenyl)dimethylsilane.[2] The latter compounds were produced by reaction of the appropriate carbanions with dichlorodimethylsilane. We now report a new approach to the synthesis of silicon-linked dithiols involving a double-Wittig (West)[4] rearrangement of easily prepared bis(alkylthio)silanes, illustrated by conversion of bis(benzylthio)dimethylsilane[5] to *d,l*- and *meso*-bis(α-mercaptobenzyl)dimethylsilane (**1**, PhCH(SH)SiMe$_2$CH(SH)Ph or H$_2$mbds) (eq 1).

$$\mathrm{PhCH_2SSiMe_2SCH_2Ph + 2RLi} \longrightarrow$$

$$\mathrm{PhCHSLiSiMe_2CHSLiPh} \xrightarrow{H^+}$$



(1)

Treatment of bis(benzylthio)dimethylsilane with 2 equivalent of *tert*-butyllithium in THF at −78 °C gave after workup *meso*- and *d,l*-**1** in 56% and 30% isolated yields, respectively, as colorless solids.[6] Ligand **1** combines a degree of steric hindrance, which allows modification of the microenvironment about a coordinated metal center to provide a binding cavity for substrate molecules, and a ligand bite distance suited to the formation of binuclear complexes. Since this latter feature is of particular interest in modeling the bimetallic activation of nitrogenous substrates by the molybdenum-containing enzyme nitrogenase,[7-9] we employ *meso*-**1** in the synthesis of a novel binuclear molybdenum complex **2**, which reacts with 1,1-methylphenylhydrazine (**3**) to give the structurally identified binuclear hydrazido(2−) species (HNEt$_3$)[Mo$_2$Cl(mbds)$_3$(NNMePh)$_2$] (**4**).

PhCH(SH)SiMe$_2$CH(SH)Ph [Mo$_2$Cl$_4$(mbds)$_3$]
1 (H$_2$mbds) **2**
(HNEt$_3$)[Mo$_2$Cl(mbds)$_3$(NNMePh)$_2$]·2CH$_2$Cl$_2$
4

The reaction of *meso*-**1** and 2 equiv of triethylamine with MoCl$_5$ in dichloromethane afforded an extremely air-sensitive species analyzying for [Mo$_2$Cl$_4$(mbds)$_3$] (**2**) as a microcrystalline brown precipitate.[10] Although solutions of **2** proved insufficiently stable

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(2) Block, E.; Gernon, M.; Kang, H.; Liu, S.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1031. Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658. Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1989**, *156*, 27. Block, E.; Gernon, M.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 1263. Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327. Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1990**, *166*, 155. Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1990**, *167*, 147.

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(4) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3222.

(5) Brandes, D. *J. Organomet. Chem.* **1976**, *105*, C1.

(6) Synthesis of **1** is as follows. Bis(benzylthio)dimethylsilane (bp 135 °C/0.1 Torr)[5] was prepared in 93‰ yield by adding Me$_2$SiCl$_2$ to a suspension of lithium α-toluenethiolate (from PhCH$_2$SH + *n*-BuLi) in hexane at 0 °C and warming the mixture to room temperature overnight. Treatment of this product with 2 equivalents of *tert*-butyllithium in THF at −78 °C followed by warming to room temperature overnight and standard workup gave a mixture of isomers of **1** in 94% yield. Recrystallization from hexane afforded *meso*-**1** as long needles (56% isolated yield), mp 97–98 °C. ^{1}H NMR: δ 7.1–7.4 (m, 10 H, phenyl), 3.39 (d, 2 H, J = 7.7 Hz, CH), 1.91 (d, 2 H, J = 7.8 Hz, SH), 0.34 (s, 3 H), −0.11 (s, 3 H). ^{13}C NMR: δ 142.59 (C), 128.29 (CH), 127.54 (CH), 125.92 (CH), 28.54 (CH), −6.60 (CH$_3$), −7.17 (CH$_3$). Anal. Calcd for C$_{16}$H$_{20}$S$_2$Si: C, 63.10; H, 6.62. Found: C, 63.18; H, 6.66. Chromatography of the mother liquor afforded *d,l*-**1** as a colorless powder (30% isolated yield), mp 65.67 °C. ^{1}H NMR: δ 7.2–7.5 (m, 10 H, phenyl), 3.72 (d, 2 H, J = 7.8 Hz, CH), 2.13 (d, 2 H, J = 7.8 Hz, SH), 0.11 (s, 6 H). ^{13}C NMR: δ 142.41 (C), 128.22 (CH), 127.61 (CH), 125.82 (CH), 28.80 (CH), −6.75 (CH$_3$). Anal. Calcd for C$_{16}$H$_{20}$S$_2$Si: C, 63.10; H, 6.62. Found: C, 63.29; H, 6.60.

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(8) Hardy, R. W. F.; Burns, R. C.; Parshall, G. W. *Adv. Chem. Ser.* **1971**, *No. 100*, 219.

(9) Coucouvanis, D.; Challin, P. R.; Koo, S.-M.; Davis, W. M.; Butler, W.; Dunham, W. R. *Inorg. Chem.* **1989**, *28*, 4183.

(10) Synthesis of **2** is as follows. Under argon, a solution of *meso*-bis(α-mercaptobenzyl)dimethylsilane (**1**) (273 mg, 0.89 mmol) and Et$_3$N (0.25 mL, 1.79 mmol) in CH$_2$Cl$_2$ (20 mL) was added slowly to a solution of MoCl$_5$ (160 mg, 0.45 mmol) in MeOH (10 mL). The resulting deep brown-red solution was stirred overnight and concentraterd to 5 mL, whereupon a fine microcrystalline brown precipitate of [Mo$_2$Cl$_4$(mbds)$_3$] (**2**) was isolated in 45% yield. Attempts to grow X-ray-quality crystals of **2** failed as a consequence of the instability of solutions of **2** in CH$_2$Cl$_2$, CH$_3$CN, or DMF. IR (KBr pellet, cm^{-1}): 1480 (m), 1445 (s), 1260 (w), 1215 (m), 1160 (m), 1100 (m), 1065 (m), 1045 (m), 800 (m), 765 (m), 695 (s), 300 (vs). Anal. Calcd for C$_{48}$H$_{54}$Si$_3$S$_6$Cl$_4$Mo$_2$: C, 46.5; H, 4.36; N, 0.00. Found: C, 46.8; H, 4.44; N, 0.00.

even at −78 °C to afford suitable crystals for X-ray analysis. **2** reacted cleanly with 2 equiv of 1,1-methylphenylhydrazine in CH_2Cl_2/methanol to yield **4**,[11] a complex that was alternatively prepared by the direct reaction of $[Mo(NNMePh)Cl_4]$[12] with *meso*-**1**.

The structure[13] (Figure 1) of the anionic species $[Mo_2Cl(mbds)_3(NNMePh)_2]^-$ consists of discrete binuclear units exhibiting the confacial bioctahedral geometry common to the $[Mo_2Cl_9]^{3-}$ class of complexes.[14] However, in contrast to the fundamental $[Mo_2X_9]^{3-}$ structural type, **4** exhibits Mo in the +5 oxidation state and three bis(thiolate) ligands each providing a bridging thiolate donor and a terminally coordinated thiolate group. The metal coordination geometries are consequently nonequivalent, with Mo1 bonding to the three bridging thiolate groups, a terminal thiolate, a chloride donor, and the nitrogen donor of one linear hydrazido(2−) ligand, while Mo2 bonds to the three bridging thiolate donors, two terminal thiolates, and the nitrogen donor of the second hydrazido(2−) ligand. Although nonequivalent metal sites are not uncommon in triply metal-metal-bonded binuclear systems of Mo(III),[15,16] binuclear complexes of Mo(V) with triple thiolate bridges exhibit more symmetrical structures.[17]

The short Mo–N and N–N distances (Figure 2) and the "linearity" of the Mo–N–N units are consistent with the description of the hydrazido(2−) fragments, -NNMePh, as four-electron donors. The strongly π-bonding hydrazido(2−) ligand exerts a considerable trans influence, as indicated by the Mo–S5 distances, which average 2.576 (8) Å compared to 2.449 (7) Å for the average of all other Mo–S distances. The observed diamagnetism of the complex is consistent with the short Mo1–Mo2 distance. The complex $[Mo_2(SCH_2CH_2S)_3(SCH_2CH_2SH)(NNPh)(NNHPh)]^{2-}$[16] exhibits gross structural features similar to those of **4**, although the presence of a terminal chloride donor and the nonequivalence of the Mo centers are unique to **4**.

Solutions of **2** are extremely sensitive to the presence of moisture or atmospheric oxygen. Introduction of oxygen to a solution of **2** in CH_2Cl_2 results in rapid color changes from the characteristic red brown of **2** to a deep purple. An infrared spectrum of the product mixture revealed the presence of both terminal and bridging oxo groups, suggesting the ubiquitous $[Mo_2O_3]^{4+}$ core. In the presence of hydrazine or acetylene, solutions of **2** turn deep red in color and the resultant microcrystalline precipitate analyzes for $(HNEt_3)[Mo_2(mbds)_3Cl_3]$ (**5**),[18] which may be structurally analogous to **4** with the hydrazido(2−) ligands replaced by chloride donors.

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Supplementary Material Available: For **4**, tables of complete atomic coordinates and thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters (9 pages); tables of structure factors (37 pages). Ordering information is given on any current masthead page.

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[11] Synthesis of **4** is as follows. All manipulations were carried out under an atmosphere of argon. (a) A solution of **2** (620 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was added to 1,1-methylphenylhydrazine (**3**) (183 mg, 1.5 mmol) and Et_3N (0.25 mL, 1.78 mmol) in CH_2Cl_2 (2 mL). After being stirred for 30 min, the solution was concentrated to 1 mL and treated with hexane (2 mL) to give a copious red-brown precipitate of **4**. Recrystallization from CH_2Cl_2/hexane afforded red crystals of **4** in 30% yield. (b) A solution of **1** (545 mg, 1.79 mmol) and Et_3N (0.5 mL, 3.58 mmol) in CH_2Cl_2 (20 mL) was added dropwise with stirring to a solution of $[Mo(NNMePh)Cl_4]$ (320 mg, 0.89 mmol) in methanol (20 mL). After the red-brown solution was stirred at room temperature for 20 h, the solvent was stripped on a rotary evaporator, resulting in the isolation of a mixture of a red-brown powder and colorless microcrystals. Washing with methanol (15 mL) removed the colorless material, whereupon the red-brown species was dissolved in CH_2Cl_2 (35 mL) and the solution carefully layered with hexane (70 mL). After 10 days, red crystals were obtained in 40% yield. IR (KBr pellet, cm^{-1}): 3065 (m), 3025 (m), 2960 (s), 2900 (sh), 2860 (w), 2840 (m), 2690 (s), 2620 (m), 1595 (s), 1500 (s), 1480 (n), 1450 (w), 1370 (s), 1340 (w), 1245 (s), 1135 (n), 1080 (n), 1040 (m), 840 (s, br), 800 (s), 780 (n), 750 (m), 720 (m), 700 (vs), 520 (w), 320 (w). Anal. Calcd for $C_{70}H_{90}N_5Si_3S_6Cl_5Mo_2$: C, 51.1; H, 5.47; N, 4.26. Found: C, 50.8; H, 5.21; N, 4.01.

[12] Kang, H.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1192.

[13] **4**·$2CH_2Cl_2$: monoclinic, space group $P2_1/c$, $a = 23.739$ (5) Å, $b = 14.537$ (3) Å, $c = 25.872$ (6) Å, $\beta = 117.09$ (2)°, $V = 7948.8$ (10) Å^3, $Z = 4$, $D_{calc} = 1.37$ g cm^{-3}; structure solution and refinement based upon 6627 reflections with $F_o \geq 6\sigma(Fo)$ (Mo Kα, $\lambda = 0.71073$ Å; 14730 total collected in the quadrant $+h, +k, \pm l$), $R = 0.069$, $R_w = 0.074$ (519 variables).

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[16] Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21.

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[18] Synthesis of **5** is as follows. Under argon, a solution of **2** (310 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was added to hydrazine (16 mg, 0.50 mmol) and Et_3N (0.25 mL, 1.78 mmol) in CH_2Cl_2 (1 mL). After being stirred overnight, the deep red solution was concentrated to 2 mL and layered with hexane (5 mL) to give a microcrystalline precipitate of **5** in 25% yield. Anal. Calcd for $C_{54}H_{70}NSi_3S_6Cl_3Mo_2$: C, 49.6; H, 5.36; N, 1.07. Found: C, 49.3; H, 5.01; N, 1.24.