Control of the Reactivity and Coordination Number of a 16-Electron Complex by π-Donating Thiolate Ligands[1]

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Abstract: The coordinatively unsaturated species $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$ (**1**) crystallizes in the monoclinic space group $C2/c$ with a = 18.712 (6) Å, b = 8.177 (3) Å, and c = 25.029 (8) Å, β = 118.30 (2)°, V = 3371.9 Å^3, Z = 8. The structure was solved by direct methods followed by least-squares refinement using 1681 independent reflections to a final R value of 0.028 (R_w = 0.034). Complex **1** was found to have unusually short Mo–S interatomic distances (2.34 Å average). The monomeric nature of **1** is surprising because most $\{MoNO\}^4$ complexes have the general formula $[M(NO)L_{7-n}]_n$ (M = a group 6 metal, L = a monodentate or bridging ligand) and exist as either coordinatively saturated seven-coordinate monomers (n = 1) or dimers (n = 2). With the aid of Fenske–Hall molecular orbital calculations, the novel stability of **1** is attributed to $p\pi$–$d\pi$ bonding interaction between the p-type lone pair on the thiolate ligands and the empty molybdenum d_{xy} orbital. This interaction simultaneously strengthens the metal thiolate bond and makes the complex less susceptible to nucleophilic attack by raising the energy of the LUMO (d_{xy}).

Several years ago McCleverty and co-workers reported the preparation of $(\eta^5\text{-}C_5H_5)Mo(NO)(SR)_2$ (**1**), R = alkyl or aryl, by treating the halide dimer $[(\eta^5\text{-}C_5H_5)Mo(NO)(I)_2]_2$ with a thiolate.[2,3] Osmometric molecular weight measurements for **1** (R = Ph) showed it to be mononuclear in nonpolar solvents.[2] The monomeric nature of **1** in solution is surprising because most $\{MoNO\}^4$ complexes[4] have the general formula $[M(NO)L_{7-n}]_n$ (M = a group 6 metal,[26] L = a monodentate or bridging ligand) and exist as either coordinatively saturated seven-coordinate monomers (n = 1) or dimers (n = 2).[2,5,6] Indeed, McCleverty and co-workers proposed that **1** adopted a binuclear structure in the solid and gas phases, in order to achieve an 18-electron configuration.[3]

Several mononuclear 16-electron molybdenum complexes have been prepared since the report of **1** by McCleverty and co-workers.[7-11] Many of the complexes are stabilized by bulky ligands.[8-11] Those 16-electron molybdenum complexes which do not contain sterically bulky ligands, such as $Mo(CO)_2(S_2CNR_2)_2$, readily add an additional ligand to form coordinatively saturated species.[7] Molecular orbital calculations by Hoffmann et al. suggest that sulfur donor atoms can also contribute to the stability of 16-electron systems.[8,9] However, stable 16-electron complexes without sterically encumbering ligands remain a rarity.

The facile formation of **1** from the disproportionation of $(\eta^5\text{-}C_5H_5)Mo(NO)_2(SC_6H_5)$ (**2**)[12] and the low reactivity of **1** with nucleophiles[13] provide further evidence that **1** has unexpected stability for a formal 16-electron complex. Related complexes of the type $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$, which contain sterically bulky alkyl groups, have recently been reported.[11] The latter complex reacts with nucleophiles and in the presence of sulfur is converted into $(\eta^5\text{-}C_5H_5)W(NO)(SCH_2SiMe_3)_2$, an analogue of **1**.[14]

Table I. Crystallographic Data for $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$ at 25 °C[a]

	Cell Parameters
formula	$C_{17}H_{15}NOS_2Mo$
fw	409.38
cryst color	dark green
cryst shape	trigonal prism
cryst size, mm	0.20 × 0.20 × 0.12
cryst system	monoclinic
space group	$C2/c$
a, Å[b]	18.712 (6)
b, Å	8.177 (3)
c, Å	25.029 (8)
β, deg	118.30 (2)
V, Å^3	3371.9
Z	8
d_{calcd}, g cm^{-1}	1.61
μ, cm^{-1}	9.968
Measurement and Treatment of Intensity Data	
radn	Mo Kα (λ = 0.71073), monochromatized by a graphite crystal
data collctn method	$\theta/2\theta$ scan
scan speed, deg min^{-1}	variable (1.0–10.0) as a function of reflection intensity
scan range (2θ), deg	Mo Kα1 −1.0 to Mo Kα2 +1.3
ratio of total bkgd time to peak scan time	0.5
std reflctns	two representative reflections recollected every 98 reflections
max deviation of stds, %	<3
max 2θ, deg	45
no. unique data	2219
no. data used	1681, $I > 3\sigma(I)$
final residuals	
R	0.028
R_w	0.034

[a] The estimated standard deviation of the least significant figure is given in parentheses in this table and in the tables that follow. [b] The cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range 7.0–23.0°.

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[1] Presented in part: Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L. "Abstracts"; XIIth International Conference on Organometallic Chemistry, Vienna, Austria, Sept 13, 1985, No. 503.

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[3] McCleverty, J. A.; Seddon, D. *J. Chem. Soc., Dalton Trans.* **1972**, 2588.

[4] Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

[5] (a) Johnson, B. F. G.; Al-Obaidi, K. H.; McCleverty, J. A. *J. Chem. Soc. A* **1969**, 1668. (b) King, R. B. *Inorg. Chem.* **1967**, *6*, 90. (c) King, R. B.; Kapoor, R. N. *J. Organomet. Chem.* **1968**, *15*, 457. (d) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1971**, 1596.

[6] James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 3308.

[7] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6568 and references contained therein. For a molecular orbital study of $Mo(CO)_2(S_2CNR_2)_2$ and related compounds, see: Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

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[9] Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kito, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* **1982**, *1*, 227.

[10] McCleverty, J. A. *Chem. Soc. Rev.* **1983**, *12*, 331 and references contained therein.

[11] Legzdins, P.; Rettig, S. J.; Sanchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

[12] Compound **2** may be prepared by treating $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$ with thiophenolate in THF (ν_{NO} (THF) 1743, 1657 cm^{-1}). Stored over an argon atmosphere, **2** decomposes over a period of several days to give **1**. Silica gel catalyzes this disproportionation. Column chromatography of **2** gives primarily **1** (yield ca. 50%) and other molybdenum-containing products that have not been isolated.

[13] Compound **1** does not react with carbon monoxide, triphenyl phosphine, or iodide. Treatment of **1** with methyl isonitrile for several days gives a mixture of products which do not appear to be the result of simple addition.

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Table II. Atomic Coordinates for the Non-Hydrogen Atoms in $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$

atom	*x*	*y*	*z*
Mo	0.81510 (2)	0.15612 (5)	0.12210 (2)
S (1)	0.86792 (7)	0.1775 (2)	0.22755 (5)
S (2)	0.67361 (7)	0.1788 (2)	0.06980 (6)
O	0.8386 (2)	0.5002 (4)	0.0980 (2)
N	0.8251 (2)	0.3653 (5)	0.1094 (2)
C(11)	0.8759 (2)	0.3865 (6)	0.2498 (2)
C(12)	0.9499 (3)	0.4440 (6)	0.2943 (2)
C(13)	0.9581 (3)	0.6015 (7)	0.3155 (2)
C(14)	0.8930 (3)	0.7052 (7)	0.2919 (2)
C(15)	0.8192 (3)	0.6497 (7)	0.2467 (2)
C(16)	0.8101 (3)	0.4913 (6)	0.2252 (2)
C(21)	0.6334 (2)	−0.0220 (6)	0.0626 (2)
C(22)	0.6476 (3)	−0.1116 (7)	0.1136 (2)
C(23)	0.6179 (3)	−0.2702 (7)	0.1064 (2)
C(24)	0.5752 (3)	−0.3378 (7)	0.0504 (3)
C(25)	0.5587 (3)	−0.2461 (8)	−0.0005 (2)
C(26)	0.5875 (3)	−0.0885 (7)	0.0057 (2)
C(31)	0.9288 (3)	0.0150 (8)	0.1330 (3)
C(32)	0.8825 (4)	−0.1007 (7)	0.1401 (2)
C(33)	0.8162 (4)	−0.1147 (8)	0.0882 (4)
C(34)	0.8204 (4)	−0.010 (1)	0.0496 (3)
C(35)	0.8880 (4)	0.0669 (8)	0.0763 (3)

Table III. Selected Interatomic Distances (Å) and Angles (deg) in $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$[a]

atoms	dist	atoms	dist
Mo–S(1)	2.345 (1)	S(1)–C(11)	1.782 (4)
Mo–S(2)	2.339 (1)	S(2)–C(21)	1.779 (5)
Mo–N	1.766 (4)	N–O	1.196 (5)
Mo–C(31)	2.320 (5)		
Mo–C(32)	2.380 (6)	S1···S2	3.898 (2)
Mo–C(33)	2.375 (7)		
Mo–C(34)	2.306 (7)		
Mo–C(35)	2.278 (6)		
atoms	**angle**	**atoms**	**angle**
S(1)–Mo–S(2)	112.66 (5)	N–Mo–Cp[a]	123.7 (1)
S(1)–Mo–N	96.1 (1)	Mo–S(1)–C(11)	110.6 (2)
S(2)–Mo–N	90.6 (1)	Mo–S(2)–C(21)	107.2 (2)
S(1)–Mo–Cp[a]	112.81 (3)	Mo–N–O	171.4 (4)
S(2)–Mo–Cp[a]	117.66 (4)		

[a] Cp is the centroid of the cyclopentadienyl ring.

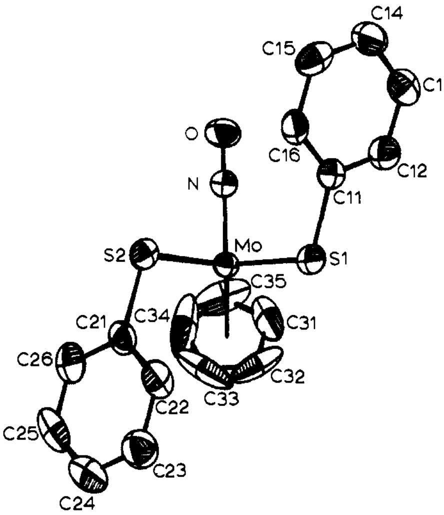


Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$. Atoms are represented by thermal vibration ellipsoids at the 50% level and the labeling scheme is defined. Hydrogen atoms have been omitted for clarity.

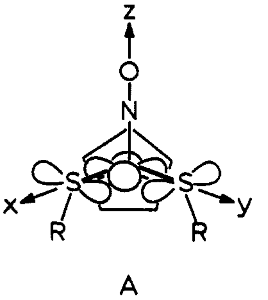
In order to better understand the novel stability of **1**, we have determined its crystal structure and investigated its electronic structure by Fenske–Hall molecular orbital calculations. The results demonstrate that **1** is monomeric in the solid state and indicate that the unusual stability of **1** is due to pπ–dπ bonding interactions between the thiolate lone pairs which are primarily sulfur 3p in character and the empty molybdenum $4d_{xy}$ orbital.

Results and Discussion

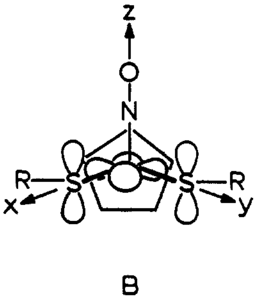
The structure of **1** (R = C_6H_5) is shown in Figure 1. Tables I–III present the crystallographic data, atomic fractional coordinates of the non-hydrogen atoms, and selected interatomic distances and angles.

The structure reveals that **1** is mononuclear and that there are no significant intermolecular contacts. The two Mo–S distances, 2.345 (1) and 2.339 (1) Å, are short compared to other examples of thiolate ligands bound to a molybdenum atom in a relatively low oxidation state. Typical molybdenum thiolate distances range from 2.33 to 2.55 Å with the short Mo–S distances associated with molybdenum atoms in high oxidation states.[15] The S–Mo–S bond angle for **1** (112.66 (5)°) is similar to that found in $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_4$ (115.3 (1)°).[8] The latter complex has been the subject of theoretical calculations which attribute the obtuse S–Mo–S bond angle to the d^4 electron configuration.[8] Other structural parameters of interest are the torsion angles which relate the rotational orientation of the thiolate ligands to the Mo–NO fragment. A R–S–Mo–NO torsion angle of 0 or 180° would orient the sulfur 3p lone pair in the *xy* plane (A). The torsion angles for **1** (R = C_6H_5) are C(11)–S(1)–Mo–NO = 12° and C(22)–S(2)–Mo–NO = 186°.

For the pseudo-octahedral geometry of **1**, the $\{MoNO\}^4$ formalism[4] predicts that the metal d_{xz} and d_{yz} orbitals will both be occupied and stabilized by dπ–pπ bonding with the empty π*(NO) orbitals, whereas the metal d_{xy} orbital will be empty. The sulfur 3p lone pair on each thiolate ligand can also undergo π-type interaction with the d_{xz}, d_{yz}, and d_{xy} orbitals of the $\{MoNO\}^4$ group; however, the nature of the π-interaction of these filled 3p orbitals on the thiolate ligands with the metal d-orbitals will depend upon the rotational orientation of the thiolate ligands. The rotational dependence of the metal thiolate bonding in **1** (R = H) was investigated by Fenske–Hall molecular orbital calculations[16,17] on conformers A and B. In A the R groups lie in the *xz* and *yz* planes and in B the R groups lie in the *xy* plane. The Mo d_{xy} orbital is shown for reference.



A



B

The results of the molecular orbital calculations are summarized in the energy level diagrams in Figure 2. The principal features of interest are the relative energies of the lowest unoccupied molecular orbital (LUMO) and the occupied molecular orbitals for conformers A and B. The energy level diagram for conformer A is shown on the left of Figure 2. In this conformation both of the thiolate ligands are oriented such that the 3p lone pairs lie in the *xy* plane. The calculation predicts that the LUMO for this conformer is 4a′, an antibonding orbital composed of the sulfur 3p lone pairs and the metal d_{xy} orbital. In conformer B the thiolate ligands are rotated by 90° so that the two sulfur 3p orbitals of

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(14) Legzdins, P.; Sanchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525.

(15) McCleverty, J. A.; Drane, A. S.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 91.

(16) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(17) Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61.

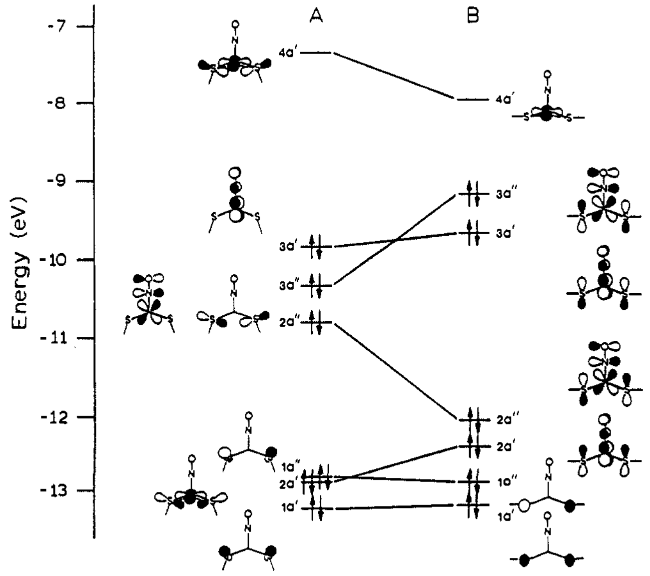


Figure 2. Energy level diagram for conformers A (left) and B (right) of $(\eta^5\text{-}C_5H_5)Mo(NO)(SH)_2$.

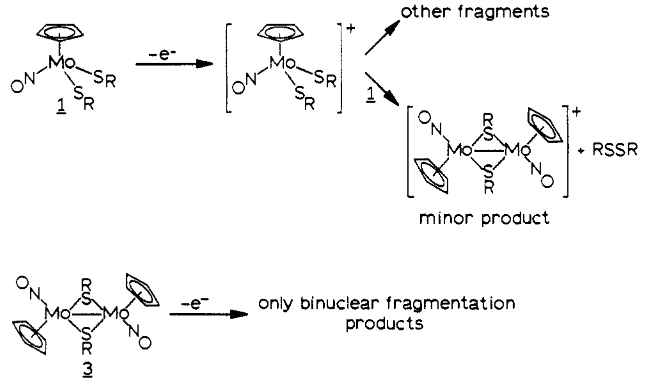
the thiolate ligands lie in the *xz* and *yz* planes. For B, the filled–filled π-interactions between the metal d_{xz} and d_{yz} orbitals and the sulfur 3p orbitals result in a net electronic destabilization of **1** relative to A. In addition, the sulfur 3p lone pairs can no longer mix with d_{xy} and as a result the LUMO (4a′) is almost entirely d_{xy}, lower in energy than for A, and presumably more accessible to incoming nucleophiles.[18] From Figure 2, conformer A is concluded to be electronically preferred and also less susceptible to nucleophiles. This conclusion is supported by the calculated total energies for A and B.[19]

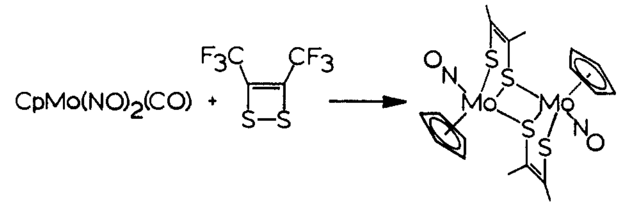
The observed X-ray structure (Figure 1) of **1** ($R = C_6H_5$) also supports the above analysis of the bonding. The small deviation of the R–S–Mo–NO torsional angles from 0 and 180° are probably due to steric and crystal packing forces.

The original study of **1** showed that it was monomeric in nonpolar solvents.[2] The crystal structure described above shows that **1** is also monomeric in the solid state, and molecular orbital calculations indicate that the monomeric structure is stabilized by the specific rotational orientations of the thiolate ligands observed in the solid-state structure of **1**. These results are not consistent with the original postulate, based upon mass spectral data, that **1** is binuclear in the gas phase.[2,3] Fortunately, the mass spectral data were published in complete detail, and it is possible to reinterpret the data in light of the additional experimental results which have appeared in the intervening years. The parent ion, $[(\eta^5\text{-}C_5H_5)Mo(NO)(SR)_2]^+$, is the most abundant ion observed in the mass spectrum of **1** ($R = C_6H_5$), but several binuclear molybdenum-containing species are observed at lower abundance, including the ion of $[(\eta^5\text{-}C_5H_5)Mo(NO)(SR)]_2$ (**3**). The observation of such binuclear ions prompted the original proposal that **1** is binuclear in the gas phase.[2,3] However, the mass spectrum reported for pure **3** does not include any of the parent ion of **1**. We suggest that the observed mass spectrum of **1** arises from the ion–molecule reactions of Scheme I which produce the ion of **3** as a minor binuclear product. This interpretation makes the gas-phase structure of **1** consistent with the monomeric structure in the solid phase and in nonpolar solvents.

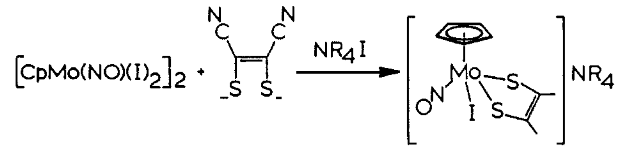
Additional information concerning the stability of **1** may be inferred from King's study of related dithiolene complexes.[20] The chelating, planar dithiolene ligand spatially orients the sulfur 3p orbitals as in conformer B, thus the dithiolene analogues of **1** exist as dimers:

Scheme I





Furthermore, McCleverty has shown seven-coordinate monomeric $\{MoNO\}^4$ dithiolene complexes are obtained in the presence of a two-electron donor:[6]



We conclude that the unusual stability of **1** results from pπ–dπ bonding between the filled sulfur 3p lone pairs and the formally empty molybdenum $4d_{xy}$ orbital. This interaction simultaneously strengthens the metal thiolate bond and makes the complex less susceptible to nucleophilic attack by raising the energy of the d_{xy} acceptor orbital.

Related studies in progress on iron thiolate complexes show that the interaction of sulfur 3p orbitals with filled metal d-orbitals can also profoundly affect the overall stability and reaction pathways of such complexes.[1,21] The consequences of these filled–filled orbital interactions will be the subject of future reports.

Experimental Section

X-ray Crystal Structure. Crystallographic data for **1** ($R = C_6H_5$) are provided in Table I. X-ray quality crystals were grown by slow evaporation of an ethyl ether solution at room temperature. Preliminary examination and data collection were performed with a Syntex $P2_1$ autodiffractometer equipped with a scintillation counter and a graphite monochromator. ω scans of several intense reflections were measured; the width at half-height was ca. 0.25° indicating good crystal quality. Examination of representative data suggested a C-centered monoclinic lattice with systematic absences *hkl* for $h + k = 2n + 1$ and *h0l* for $l = 2n + 1$, and, from subsequent least-squares refinement, the space group was determined to be $C2/c$ (No. 15). A unique quadrant of data was collected at room temperature using a $\theta/2\theta$ scan technique and Mo Kα radiation. The scan rate varied from 1.0 to 10.0 deg/min (in ω) as a function of peak intensity. A total of 2498 reflections were collected of which 2219 were unique and not systematically absent. Lorentz and polarization corrections were applied to the data; however, no absorption correction was applied. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of 131 observed and accepted reflections were 2.5% on the basis of intensity and 2.1% on the basis of F_o.

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[18] Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441.

[19] The calculated approximate total energy for conformer A is −103.302 au and for B is −103.034 au.

[20] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1967**, *6*, 469.

[21] Ashby, M. T.; Enemark, J. H. "Abstracts"; XIIth International Conference on Organometallic Chemistry, Vienna, Austria, Sept 8, 1985, No. 65.

The structure determination and subsequent refinement were carried out by using the SDP series of crystallographic programs[22] running interactively on a PDP 11/34a computer. The positions of the heavy atoms were determined by direct methods, and the remaining atoms, including the hydrogen atoms, were located in succeeding difference Fourier syntheses. The hydrogen atoms were assigned an arbitrary isotropic thermal parameter of $B = 5.0$ Å^2 and included as fixed contributors in the final structure factor calculations. Neutral atomic scattering factors were taken from Cromer and Waber.[23a] The effect of the real and imaginary components of anomalous dispersion for the molybdenum and sulfur atoms were included in the structure factor calculations using the tabulated values of Cromer.[23b] Only the 1681 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The final cycles of refinement included 199 variable parameters and converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.028$ and $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum wF_o^2)]^{1/2} = 0.034$ where $w = 4F_o^2/[\sigma^2(F_o^2)+(pF_o^2)^2]$ and p, the factor to prevent overweighting of the strong reflections, was set equal to 0.03. The highest peak in the final difference electron density map had a height of 0.28 e Å^{-3}. Plots of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indicies showed no unusual trends.

Molecular Orbital Calculations. Orbital eigenvalues were calculated by the Fenske–Hall self-consistent-field (SCF) method.[16,17] Atomic basis functions of Richardson[24] were used for molybdenum (with a 5s exponent of 2.0 and a 5p exponent of 1.8) and Clementi[25] for carbon, nitrogen, oxygen (all with double-ζ functions with 1s and 2s reduced to single-ζ form), and sulfur (with double-ζ functions with the 1s, 2s, 2p, and 3s reduced to single-ζ form). An exponent of 1.2 was used for the hydrogen atom. Optimized bond lengths and angles were obtained from the X-ray crystal structure determination of **1** ($R = C_6H_5$). To simplify the calculations, the aryl rings were replaced with hydrogen atoms. A S–H bond length of 1.5 Å, a Mo–S–H bond angle of 120°, and a S–Mo–S bond angle of 90° were used. Furthermore, the cyclopentadienyl ring was constrained to D_{5h} symmetry with a C–C distance of 1.43 Å and a C–H distance of 1.09 Å. The coordinate system oriented the two thiolate ligands along the x and y axes and the nitrosyl ligand along the z axis. The calculations were carried out for conformers A and B. In A the R groups lie in the xz and yz planes and in B the R groups lie in the xy plane. For B, one anti and two syn conformers are possible. One of the syn conformers was chosen for the calculations in order to simplify the energy level diagram. The crystal structure is of the less sterically demanding anti isomer.[26]

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Supplementary Material Available: A listing of the anisotropic thermal parameters, hydrogen atom fractional coordinates, and structure factors for $(\eta^5\text{-}C_5H_5)Mo(NO)(SC_6H_5)_2$ (13 pages). Ordering information is given on any current masthead page.

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[22] Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazelkamp, R., vanKonigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

[23] (a) Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a, p 149. (b) Cromer, D. T. *Ibid.* Table 2.3.1, p 72.

[24] Richardson, J. W.; Niewpoort, W. C.; Powell, R. R.; Edgell, W. E. *J. Chem. Phys.* **1962**, *36*, 1057.

[25] Clementi, E. *J. Chem. Phys.* **1964**, *40*, 1944.

[26] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Titanacyclobutanes Derived from Strained Cyclic Olefins: The Living Polymerization of Norbornene

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Abstract: Bis(cyclopentadienyl)titanacyclobutanes **1** and **3** have been prepared from the reaction of norbornene (bicyclo[2.2.1]hept-2-ene) with precursors of "$Cp_2Ti{=}CH_2$" and "$Cp_2Ti{=}CHC(CH_3)_2CHCH_2$", respectively. On thermolysis, both **1** and **3** produce products consistent with the intermediacy of α-substituted titanocene carbene compounds. Thermolysis at 65 °C in the presence of excess norbornene affords ring-opened polynorbornene with a cis to trans ratio of 38:62. The polymerizations are highly efficient in catalyst and yield polymers of controlled molecular weight. Polymer prepared from **3** shows polydispersities as low as 1.08 based on gel permeation chromatography vs. polystyrene standards. The molecular weight distributions of polymers obtained with **1** are always broader than those obtained with **3**. The kinetics of both polymerizations are zero order in monomer with $\Delta G^{\ddagger}_{338} = 24$ kcal/mol, $\Delta H^{\ddagger} = 27$ kcal/mol, and $\Delta S^{\ddagger} = 9$ eu. Polymerization with **1** shows an induction period corresponding to a first-order decay of **1** with $t_{1/2} = 80$ min at 65 °C, whereas the polymerization with **3** is linear throughout. Simultaneous incorporation of norbornene-d_2 into the polymer by all active sites confirms that this system is best described as a living polymer. The polymerization mechanism is discussed as an olefin metathesis with rate-limiting cleavage of trisubstituted titanacyclobutanes affording high-energy carbene intermediates.

The ring-opening polymerization of cyclic olefins[1] is an important application of the olefin metathesis reaction.[2] Several ring-opened polymers, including *trans*-polyoctenamer[3] and polynorbornene,[4] currently are produced industrially. While a variety of metal systems catalyze ring-opening polymerization, the details of their initiation and propagation have not been firmly established.

The work in this group has dealt with the chemistry of bis(η^5-cyclopentadienyl)titanacyclobutane compounds.[5] These sys-

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[3] Streck, R. *CHEMTECH* **1983**, *13*, 758 and ref 2a, p 331.

[4] Ohm, R.; Stein, C. In "Encyclopedia of Chemical Technology", 3rd ed.; Grayson, M., Ed.; Wiley-Interscience: New York, 1982; Vol. 18, pp 436–442.

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