by the method of Gastro and Stephens.[28] The p-substituted iodobenzenes were all obtained from Pfaltz and Bauer and used without further purification. Iodomesitylene was prepared from mesitylene, ICl, and $\mathrm{ZnCl_2}$ by the literature method; mp 31 °C (lit 32 °C).[33] In all cases the resulting acetylene was recrystallized from methanol or hexanes until no change in melting point was observed. p-$\mathrm{ClC_6H_4C{\equiv}CPh}$: mp 80.5–81.5 °C (lit.[29] 81.5–82 °C); IR($\mathrm{CCl_4}$) 2225 (w), 1605 (sh), 1595 (s), 1495 (s), 1445 (s), 1400 (s), 1090 (s), 1015 (s), 825 (s), 685 (s) $\mathrm{cm^{-1}}$. p-$\mathrm{CH_3C_6H_4C{\equiv}CPh}$: mp 70–71 °C (lit.[30] mp 72–74 °C); IR($\mathrm{CCl_4}$) 2215 (w), 1600 (s), 1515 (s), 1487 (s), 1445 (s), 685 (s) $\mathrm{cm^{-1}}$; ^{1}H NMR($\mathrm{C_6D_6}$) δ 1.99 (s, 3 H), 6.97 (m, 5 H), 7.50 (m, 4 H). p-$\mathrm{MeOC_6H_4C{\equiv}CPh}$: mp 57–61 °C (lit.[30,31] mp 58–60 °C); IR($\mathrm{CCl_4}$) 2210 (w), 1500 (s), 1435 (m), 1242 (s), 1168 (m), 1030 (s), 825 (s) $\mathrm{cm^{-1}}$; ^{1}H NMR($\mathrm{C_6D_6}$) δ 3.17 (s, 3 H), 6.5–7.4 (m, 9 H). p-$\mathrm{NO_2C_6H_4C{\equiv}CPh}$: mp 117–118 °C (lit.[30] mp 119–120 °C); IR($\mathrm{CCl_4}$) 2225 (m), 1600 (s), 1528 (s), 1350 (s), 855 (s), 689 (s) $\mathrm{cm^{-1}}$. 2,4,6-$\mathrm{C_6H_2(CH_3)_3C{\equiv}CPh}$: mp 36.5–37 °C (lit.[34] 36–37 °C); IR($\mathrm{CCl_4}$) 3100–2910 (mult, s), 2210 (m), 1612 (s), 1598 (s), 1495 (s), 850 (s), 685 (s) $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 2.10 (s, 3 H), 2.48 (s, 6 H), 6.71 (s, 2 H), 7.0 (m, 3 H), 7.48 (m, 2 H).

Acknowledgment. We are grateful to Dr. Richard Marsh (California Institute of Technology) for extensive assistance with the X-ray diffraction study. We also acknowledge the assistance of Mr. Rudi Nunlist in the NMR experiments and stimulating correspondence on the mechanism of insertion reactions with Professors H. C. Clark and M. L. H. Green. Financial support for this work was provided by the National Institutes of Health (Grant No. GM-12459).

---

(28) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.

(29) Newman, M. S.; Reid, D. E. *J. Org. Chem.* **1958**, *23*, 665.

(30) Scandiglia, F.; Roberts, J. D. *Tetrahedron* **1958**, *3*, 197.

(31) Katritzky, A. R.; Boulton, A. J.; Short, D. J. *J. Chem. Soc.* **1960**, 1519.

(32) Ito, T.; Kirayama, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3250.

(33) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1956**, *78*, 5623.

(34) Martelli, P. G.; Spangnolo, P.; Trecco, M. *J. Chem. Soc. B* **1970**, 1413.

(35) Pouchert, C. J.; Campbell, "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1974; Vol. 1–25 D.

(36) Rummens, F. H. A.; Dehaan, J. W. *Org. Magn. Reson.* **1970**, *2*, 351.

A Novel Molybdenum Thiolato Compound, Tetrakis(*tert*-butylthiolato)molybdenum(IV). Preparation and Crystal and Molecular Structure

Sei Otsuka,*[1a] Masato Kamata,[1a] Ken Hirotsu,[1b] and Taiichi Higuchi*[1b]

Contribution from the Departments of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan, and the Osaka City University, Sumiyoshiku, Osaka 558, Japan. *Received October 27, 1980*

Abstract: The new dark red, diamagnetic Mo(t-BuS)$_4$ was prepared by treating anhydrous $\mathrm{MoCl_4}$ with t-BuSLi in 1,2-dimethoxyethane (>45% yield). The molecular structure has been determined by a single-crystal X-ray analysis. The compound crystallizes in tetragonal space group $P4_22_12$ with a = 10.975 (1) Å, c = 10.249 (1) Å, and with two molecules in a unit cell. The structure, solved by the heavy-atom method, was refined to R = 0.065 for 578 reflections. The geometry of sulfur atoms around Mo(IV) has an approximately D_{2d} configuration with two distinct SMoS angles (average 116.9 and 95.6°) and a single MoS distance (2.235 (3) Å).

So far homoleptic tetracoordinate molybdenum(IV) compounds $\mathrm{MoL_4}$ remain a rarity. Thermally stable $\mathrm{Mo(NR_2)_4}$ (R = Me, Et) and relatively unstable $\mathrm{Mo(OR)_4}$ (R = t-Bu, t-$\mathrm{BuCH_2}$) derived therefrom are well-known[2,3] and constitute rare examples of monomeric, diamagnetic tetracoordinate d^2 ions. Conspicuously, tetrakis(thiolato)molybdenum(IV) compounds have not been reported yet. Closely related may be $\mathrm{Mo(SCH_2CH_2SCH_2CH_2S)_2}$ which is, however, a hexacoordinate trigonal prismatic Mo(IV) compound.[4] We have been interested in obtaining $\mathrm{Mo(SR)_4}$ since it would serve as a potential starting material for molybdenum sulfur compounds having no oxo ligands. In the molybdenum–sulfur chemistry, chelating disulfur ligands such as dithioacid (dithiocarbamate and xanthate) or dithiolate are commonly used.[5] Complexes thus obtained assume higher coordination numbers than four[5] and in general are rather inert. So that a new thiolato molybdenum family having no oxo ligands could be developed, more labile sulfur complexes are apparently needed as starting material. This paper describes the first successful preparation of a tetrakis(thiolate) compound, Mo(t-BuS)$_4$, and its molecular structure as determined by a single-crystal X–ray analysis. This compound indeed was found to be substitution active providing accesses to a variety of molybdenum thiolate compounds.

Experimental Section

Physical Measurements. All manipulations of air-sensitive molybdenum complexes were carried out under a nitrogen atmosphere. IR and UV–visible spectra were recorded on a Hitachi Model 295 and Hitachi EPS-3T spectrometer, respectively. ^{1}H NMR were recorded with a Jeol JNM-4H-100 or Jeol JNM-PMX-60. Cyclic voltammetric measurements were made with a Hokuto Denko Potentiostat Model HA-201 at 25 °C with use of DMF solutions containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Materials. Anhydrous $\mathrm{MoCl_4}$ was prepared from $\mathrm{MoCl_5}$ (Climax Molybdenum Co.) according to a literature method.[6] *tert*-Butyl mercaptan (Nakarai Chemical Co., Ltd.) was distilled before use. *tert*-Butyl

---

(1) (a) Osaka University. (b) Oska City University.

(2) Chisholm, M. H.; Reichert, W. W.; Thornton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744 and references cited therein.

(3) For reviews see: (a) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. (b) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259. (c) Bradley, D. C.; Fisher, K. J. *Int. Rev. Sci.: Inorg. Chem., Ser. One*, **1972**, *5*, 65.

(4) Hyde, J.; Magin, L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 204.

(5) (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301. (b) Willemse, J.; Cras, J. A.; Steggerda, J. J.; Keijzers, C. P. *Struct. Bonding* **1976**, *28*, 83.

(6) Kepert, D. L.; Mandyczewsky, R. *Inorg. Chem.* **1968**, *7*, 2091.

0002-7863/81/1503-3011$01.25/0

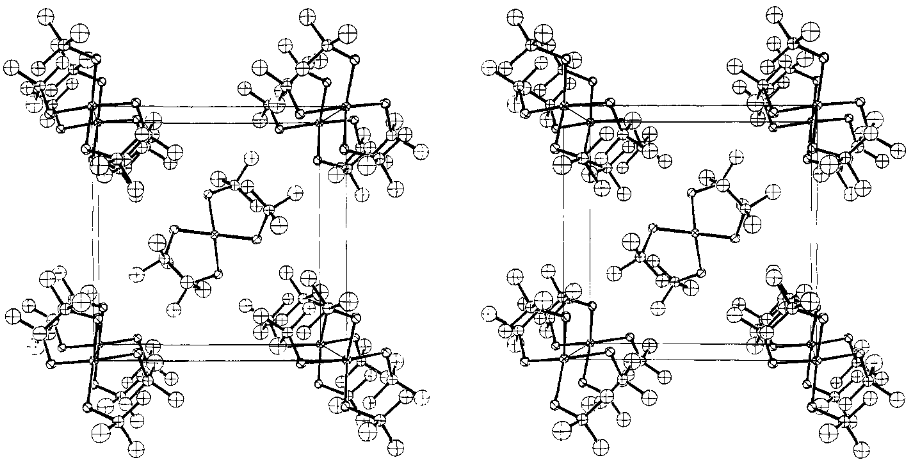


Figure 1. Stereodiagram of one unit cell showing the packing of $Mo(t\text{-}BuS)_4$. The view is down the *c* axis with *b* axis vertical.

isocyanide was prepared by the method described previously.[7] All the solvents were dried with appropriate desiccants (sodium, calciumhydride or P_2O_5) and distilled under a nitrogen atmosphere.

Preparation of $Mo(t\text{-}BuS)_4$. To a THF (20 mL) solution of *t*-BuSH (10.8 g, 120 mmol) was added slowly at 0 °C a hexane solution (75 mL) of *n*-BuLi (1.6 M); the resultant solution was stirred for 30 min. THF was added to the solution to make the total volume 120 mL. This solution was used as a 1.0 M solution of *t*-BuSLi. A 1.62-g (6.81 mmol) sample of $MoCl_4$ was dissolved in 60 mL of 1,2-dimethoxyethane (DME) while the temperature was kept below 5 °C by an ice bath. To the solution cooled at 0 °C was added while stirring 30 mL of the above 1.0 M solution of *t*-BuSLi, and the stirring continued for 4 h. The dark reddish violet reaction mixture was evaporated to dryness under vacuum, and the residue was extracted with hexane several times. Complete removal of the solvent from the filtered extract gave a dark red solid material. Recrystallization of this material with the use of a small amount of hexane at 0 °C gave pure $Mo(t\text{-}BuS)_4$ in +45% yield; red prism, mp 108 °C dec. It sublimes at 70 °C (10^{-3} torr). Anal. Calcd for $C_{16}H_{36}S_4Mo$: C, 42.46; H, 8.02. Found: C, 42.11, H, 8.10.

X-ray Crystallographic Procedure. A dark red tabular crystal (0.35 × 0.21 × 0.10 mm) grown from hexane was carefully sealed in a Lindemann capillary under a nitrogen atmosphere and used to obtain X-ray data which were recorded on a Philips PW1100 four-circle diffractometer with use of graphite monochromatic Mo Kα (0.7107 Å) radiation and a ω–2θ scan technique. The observed systematic absences are *h*00 for *h* odd and 00*l* for *l* odd, consistent with space group $P4_22_12$. The cell constants, determined by a least-squares fit of 18 2θ values, were a = 10.975 (1) and c = 10.249 (1) Å. The experimental and calculated (Z = 2) densities of, respectively, 1.18 and 1.217 g/cm^3 indicated $^1/_4$ molecule $Mo(SC(CH_3)_3)_4$/asymmetric unit. All unique diffraction maximum with $2\theta < 55°$ were collected. Three reference reflections monitored every 180 min displayed neither systematic nor significant deviations from their initial intensities. Of the 872 reflections surveyed in this manner, 578 (66.3%) had $I > 3\sigma(I)$ and were classified as observed. The intensities were corrected for Lorentz and polarization factors, but an absorption correction was not made. The structure was solved by the usual heavy-atom procedure: deconvolution of a Patterson function to reveal the Mo and the S positions and location of nonhydrogen atoms in a subsequent electron density synthesis. The structure was refined by full-matrix least-squares techniques, minimizing the function $w(|F_o| - |F_c|)^2$; the weights were assigned as $1.0/\sigma(F_o)^2$. R and R_w were 0.099 and 0.110 after three cycles of isotropic least-squares refinement. Six cycles of refinement with anisotropic temperature factors for the Mo, S, and isotropic C atoms converged to $R = 0.065$ and $R_w = 0.088$.[8] Neutral atomic scattering factors of Cromer and Waber[9] were used for all atoms. They were all corrected for the real part of the anomalous dispersion.

Table I. UV-Visible Spectrum of $Mo(t\text{-}BuS)_4$[a]

λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
238	25000	420	7200
282	23000	518	1100
320 sh	4300	720	1500
355 sh	3200		

[a] In hexane.

Fractional coordinates and thermal parameters are listed in Table II. The important bond lengths and bond and dihedral angles are shown in Table III. A table of structure factors is available as supplemental material.

Results and Discussion

Preparation. $MoCl_4$ in 1,2-dimethoxyethane reacts readily with *t*-BuSLi at low temperature according to eq 1. The isolation of

$$MoCl_4 + 4t\text{-}BuSLi \rightarrow Mo(t\text{-}BuS)_4 + 4LiCl \qquad (1)$$

$Mo(t\text{-}BuS)_4$ can be achieved through hexane extraction with satisfactory yield (>45%). The preparative success depends greatly on the choice of solvent; e.g., the reaction in THF gave a much poorer yield. Anhydrous and anaerobic conditions are necessary for the successful snythesis.

An obvious alternative prepartion of this compound, substitution reaction of the known compound $Mo(NMe_2)_4$[3], was attempted. Thus the reaction with a slight excess of *t*-BuSH carried out in pentane (28 °C, 5 h) followed by usual workup was found to produce the compound in a low yield (<15%) (eq 2). In view

$$Mo(NMe_2)_4 + 4t\text{-}BuSH \rightarrow Mo(t\text{-}BuS)_4 + 4Me_2NH \qquad (2)$$

of the rather poor yield (~22%) for the preparation of the starting compound $Mo(NMe_2)_4$, this route does not seem to be useful. It is notable that with less bulky sulfides such as *i*-PrS$^-$ or EtS$^-$ the similar preparation merely results in a mixture of ill-defined polymeric molybdenum thiolate compounds.

The dark red diamagnetic $Mo(t\text{-}BuS)_4$ is sensitive to air and moisture and sublimes at 70 °C (10^{-3} torr). The UV-visible spectrum is characterized with two distinct absorptions at 238 (ϵ 2.5 × 10^4) and 282 nm (ϵ 2.3 × 10^4 M^{-1} cm^{-1}) accompanied by two weaker absorptions at ~320 and 355 nm. Several absorptions appear in the visible to far-infrared region (Table I). The IR spectrum of this compound shows bands at 465 and 435 cm^{-1}, characteristic of ν(Mo–S), and at 1150 cm^{-1}, attributed to δ(C–C–CH$_3$). The ^1H NMR spectrum (C_6D_6) shows a sharp singlet at δ 1.58 due to the *tert*-butyl proton consistent with the diamagnetism, no other signal being detected. The diamagnetism invokes a distortion from the regular tetrahedron. This was confirmed by an X-ray analysis as will be described below.

The redox properties were briefly studied by cyclic voltammetry. In DMF solution (1.0 mM), an irreversible reduction was observed

---

[7] Otsuka, S.; Mori, K.; Yamagami, K. *J. Org. Chem.* **1966**, *31*, 4170.

[8] Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFLS, A Fortran Crystallographic Least Square Programme"; U. S. Atomic Energy Commission Report ORNL-TM-305; Oak Ridge National Laboratory, Oak Ridge, TN, 1970. Johnson, C. A. "ORTEP-II, A Fortran Thermal Ellipsoid Plot Programme for Crystal Structure Illustrations"; U.S. Atomic Energy Commission Report ORNL-3794 (2nd revision with supplemental instructions); Oak Ridge National Laboratory, Oak Ridge, TN, 1971. Sakurai, T., Ed. "UNICS, The Universal Crystallographic Computation Program System"; The Crystallographic Society of Japan: Tokyo, Japan, 1967.

[9] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, p 72.

Table II. Positional and Thermal Parameters[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0	0	0	46 (1)	46 (1)	43 (1)	1 (1)	0	0
S	−213 (3)	−1722 (3)	1141 (3)	55 (3)	61 (2)	63 (2)	−5 (2)	−9 (2)	13 (2)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
C(1)	986 (15)	−2149 (15)	2310 (16)	74 (5)	C(3)	352 (25)	−2450 (25)	3503 (26)	166 (10)
C(2)	1953 (18)	−1240 (20)	2535 (20)	106 (7)	C(4)	1692 (22)	−3281 (22)	1796 (21)	145 (8)

[a] The fractional atomic coordinates are × 10^4 with the thermal parameters given in Å × 10^3. The U_{ij} coefficients are given by the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Estimated standard deviations are given in parentheses for the least significant figures.

Table III. Selected Bond Lengths (Å) and Bond and Dihedral Angles (Deg)

(a) Bond Distances			
Mo–S	2.235 (3)	C(1)–C(3)	1.45 (3)
S–C(1)	1.84 (2)	C(1)–C(4)	1.56 (3)
C(1)–C(2)	1.48 (3)		
(b) Intramolecular Short Contacts			
S- - -S′	3.809 (5)	Mo- - -C(1)	3.51 (2)
S- - -S″	3.311 (5)	Mo- - -C(2)	3.63 (2)
S- - -S‴	3.806 (5)		
(c) Bond Angles			
S–Mo–S′	116.9 (1)	S–C(1)–C(3)	105.4 (15)
S–Mo–S″	95.6 (1)	S–C(1)–C(4)	109.8 (13)
S–Mo–S‴	116.8 (1)	C(2)–C(1)–C(3)	111.6 (18)
Mo–S–C(1)	118.8 (6)	C(2)–C(1)–C(4)	103.6 (16)
S–C(1)–C(2)	116.4 (13)	C(3)–C(1)–C(4)	110.1 (18)

(d) Dihedral Angles between Planes[b]

plane	plane	angle
S–Mo–S″	S′–Mo–S″	89.9
Mo–S–C(1)	Mo–S′–C(1)′	87.9
Mo–S–C(1)	Mo–S″–C(1)″	177.7
Mo–S–C(1)	Mo–S‴–C(1)‴	80.8

[a] S′, atom with coordinates $-x, -y, z$. S″, atom with coordinates $y, x, -z$. S‴, atom with coordinates $-y, -x, -z$. [b] The five atoms C(1)–S–Mo–S″–C(1)″ lie approximately coplanar, deviation (Å) of atoms from the least-squares plane being S, 0.017; C(1), −0.008; S″, −0.017; C(1)″, 0.008. Plane C(1)′–S′–Mo–S‴–C(1)‴ is symmetrically equivalent with the above plane.

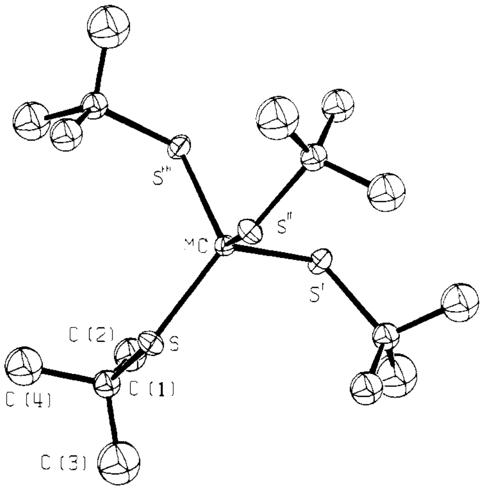


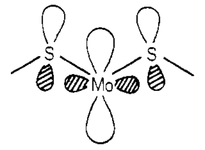
Figure 2. Perspective view of the complex molecule showing the atomic numbering.

at −1.17 V (vs. SCE, scan rate 100 mV/s). No identifiable product was isolated by the electrochemical reduction.

Despite a great deal of recent attention on the chemistry of molybdenum compound with sulfur-containing ligands due to their possible implications in the redox-active molybdo enzymes,[4,10,11] this type of simple tetrakis(thiolate)molybdenum(IV) compounds has not been made prior to this work. Thus its molecular structure and reactivity deserve scrutiny. This compound proved to be a versatile starting compound for preparation of a wide range of new thiolato-molybdenum complexes. For example, it readily reacts with an alkyl isocyanide to give the hexacoordinate Mo(II) compound $Mo(t\text{-}BuS)_2(RNC)_4$ which is also substitution active, as will be described separately.

X-ray Structure. Present crystal structure analysis unambiguously establishes this compound to be monomeric. The molecular packing in a unit cell is shown in Figure 1 and the molecular geometry with the atomic numbering scheme in Figure 2. The shortest intermolecular distance was 3.64 Å (C(4)---C(2)). Since the Mo atoms lie on special positions, the whole complex molecule has a crystallographic symmetry of D_2. The Mo atom is coordinated by four S atoms in a distorted (elongated) tetrahedral environment (Figure 2). The MoS_4 moieties have nearly perfect D_{2d} symmetry with two distinct SMoS angles (average 116.9 and 95.6°, Table II).

The dihedral angle between planes S–Mo–S″ and S′–Mo–S‴ is 89.9° (Table III). A set of nearly coplanar five atoms C(1)–S–Mo–S″–C(1)″ or C(1)′–S′–Mo–S‴–C(1)‴ forms a W shape with a narrower S–Mo–S angle of 95.6°. An interaction between the sulfur lone pair orbitals with the vacant d_{z^2} of Mo atom may be invoked to account for the W form as depicted schematically (I). Note that a wide S–Mo–S angle disfavors such π interactions. A similar interaction has been suggested for $Mo(NMe_2)_4$.[12] The driving force to distort the regular T_d structure of d^2 ions to D_{2d} configuration cannot be ascribed to the Jahn–Teller effect.[13] The spin-paired ground state, as is frequently found in second- and third-row metal complexes, is probably a reflection of the spin-pairing energies (e.g., Cr > Mo) and the ligand field energies (e.g., Mo > Cr)[2].



I

The Mo–S–C(1) and S–C(1)–C(2) bond angles of, respectively, 118.6 and 116.4° are somewhat larger than usual apparently due to the nonbonded repulsion of Mo---C(2) (3.63 Å). The Mo–S bond length of 2.235 (3) Å is shorter than the Mo^{IV}–S single bond (2.419–2.576 Å) found in $MoO(S_2CN(C_3H_7)_2)_2(TCNE)$,[14a] $Mo(\eta\text{-}C_5H_5)_2(o\text{-}S_2C_6H_4)$,[14b] $Mo(\eta\text{-}C_5H_5)_2$(toluene-3,4-dithiolate),[14c] and $Mo(S_2CNEt_2)_4$[14d] and even shorter than that (2.361 Å) found for the closely related compound $Mo(SCH_2CH_2SCH_2CH_2S)_2$.[3] The covalent radius of a metal ion is susceptible to the change in hybridization;[15] a lower coordination number generally results in a shorter metal–ligand distance.[16] Thus, it

---

(10) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

(11) Newton, W. E.; Otsuka, S., Ed. "Molybdenum Chemistry of Biological Significance"; Plenum Press: New York, 1980.

(12) Chisholm, M. H.; Cotton, F. A.; Extine, N. W. *Inorg. Chem.* **1978**, *17*, 1329.

(13) Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 2741.

(14) (a) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99. (b) Kutoglu, A.; Koepf, H. *J. Organomet. Chem.* **1970**, *25*, 455. (c) Knox, J. R.; Pront, C. K. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2013. (d) Van der Aalsvoort, J. G. M.; Beurskens, P. T. *Cryst. Struct. Commun.* **1974**, *3*, 653.

(15) Mason, R. *Chem. Soc. Rev.* **1972**, *1*, 431.

is reasonable that compared to mercapto–Mo(IV) complexes of higher coordination numbers, the Mo(IV)–S(mercapto) distance of Mo(t-BuS)$_4$ is shorter.

Since the molecular structure of tetrakis(alcoholato)molybdenum(IV) compound has not been studied by X-ray diffraction, this work contributes to our knowledge on the structural chemistry of the rather rare class of mononuclear tetracoordinate d^2 species. The electronic structure of Mo(t-BuS)$_4$, as studied by a UV photoelectron spectroscopy and X$_\alpha$-SW MO calculations, will be a subject of a separate paper.

Acknowledgment. We thank Japan Synthetic Rubber Co., Ltd., for the partial financial support and Climax Molybdenum Co. for the generous gift of molybdenum pentachloride.

Supplementary Material Available: Table listing observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

---

(16) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

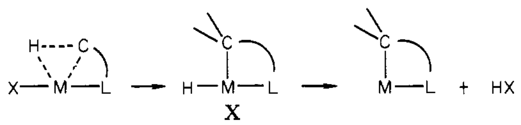
Structures, Spectroscopy, and a Mechanism of Formation of Linked-Norbornadiene Complexes of Ruthenium(II). Interaction of Ruthenium(II) with Alicyclic Hydrogen Atoms

Kenji Itoh,[†] **Noriaki Oshima,**[†] **Geoffrey B. Jameson,**[‡] **Huntley C. Lewis,**[‡] **and James A. Ibers***,[‡]

Contribution from the Toyohashi University of Technology, School of Materials Science, Tempaku-cho, Toyohashi, 440 Japan, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received July 23, 1980*

Abstract: Reduction of [RuCl$_2$(diene)]$_n$ (diene = norbornadiene (bicyclo[2.2.1]hepta-2.5-diene) or 1,5-cyclooctadiene) by means of zinc powder in the presence of norbornadiene (NBD) in refluxing acetonitrile affords a mixture of two new ruthenium(II) complexes of empirical formula RuClC$_{21}$H$_{25}$, in which three NBD molecules are involved. The structures of the cocrystallizing complexes [bicyclo[2.2.1]hepta-2,5-diene-(2,3,5,6-η)]chloro[3-(tricyclo[2.2.1.0^{2,6}]heptan-3-yl-κH^3)-*endo,endo*-bicyclo-[2.2.1]hept-5-en-2-yl-(2,5,6-η)]ruthenium(II) and [bicyclo[2.2.1]hepta-2,5-diene-(2,3,5,6-η)][*endo*-3-(bicyclo[2.2.1]hept-5-en-2-yl-κH^2)-*endo,endo*-bicyclo[2.2.1]hept-5-en-2-yl-(2,5,6-η)]chlororuthenium(II) were determined by single-crystal X-ray diffraction methods. These two isomers, differing only in the nature of the third noncoordinated NBD moiety, were found in the crystal in a ratio 86:14, respectively. Proton NMR spectroscopy of these complexes indicates a strong interaction between the ruthenium(II) atom and a hydrogen atom of the hydrocarbon ligand (δ −3.74 for the major isomer, δ −2.83 for the minor isomer), which was further substantiated by the X-ray structure determination of this complex. Relevant crystal data are as follows: space group C_i^1—$P\bar{1}$; a = 7.389 (2), b = 13.271 (4), c = 9.439 (3) Å; α = 105.37 (2)°, β = 101.18 (2)°, γ = 92.80 (2)°; V = 861.3 Å^3 at −150 °C; Z = 2; ρ_{obsd} = 1.59 (1), ρ_{calcd} = 1.590 g cm^{-3}. The molecules, including hydrogen atoms, were refined on F^2, including $F_o{}^2 < 0$ (6762 unique data collected at −150 °C), to values for R and R_w on F^2 of 0.050 and 0.072. For the portion of data where $F_o{}^2 > 3\sigma(F_o{}^2)$ (5788 reflections), the values for R and R_w on F are 0.028 and 0.036. The primary coordination sphere is composed of one chloro, one alkyl, and three olefin ligands. Two metal–olefin bonds are provided by a free norbornadiene molecule. The third such bond is provided by a substituted norbornenyl molecule; the other olefin bond of its norbornadiene parent is now involved in (i) a metal–alkyl bond approximately trans to the chloro ligand and in (ii) a covalent bond to a nortricyclyl derivative of norbornadiene for the major component and a (second) norbornenyl derivative for the minor component. A pseudooctahedral geometry is completed by an unusually close Ru···HCR$_3$ contact of 2.10 (3) Å with the otherwise dangling nortricyclyl (or norbornenyl) component. The Ru–Cl separation is 2.483 (1) Å; the Ru–C$_{sp^3}$ separation is 2.099 (2) Å, and the six Ru–C$_{\text{olefin}}$ separations range from 2.110 (2) to 2.353 (2) Å. The C=C bond lengths (1.422 (2), 1.400 (2), and 1.385 (2) Å) are correlated with the Ru–C$_{\text{olefin}}$ separations. For the related complex [Ru(C$_{21}$H$_{25}$)(CH$_3$CN)][CF$_3$SO$_3$], generated by the reaction of RuClC$_{21}$H$_{25}$ with silver triflate in an acetonitrile solution, an even stronger interaction between the ruthenium(II) center and the hydrogen atom was inferred from the ^{1}H NMR spectrum (δ −4.93). Formation of the RuClC$_{21}$H$_{25}$ moiety from the active intermediate complex RuHCl(NBD)$_2$ by an Ru–H insertion followed by an Ru–C insertion into olefinic bonds is postulated.

Activation of carbon–hydrogen bonds by means of transition-metal complexes has attracted much attention in recent years because of its importance in homogeneous catalysis and in stereoselective, transition-metal-mediated, carbon–carbon bond formation.[1,2] A well-known example of carbon–hydrogen bond activation occurs in the orthometalation of C–H bonds of aryl-substituted phosphorus[1-3] and nitrogen ligands.[4] Activation of aliphatic carbon–hydrogen bonds of tolyl-[5,6] and alkylphosphine[6-8] ligands have also been reported. A schematic diagram of such activation is shown in eq 1.



(1)

Most C–H bond activation so far studied has been assisted by this "template effect" of the donor nitrogen or phosphorus atoms.

[†] Toyohashi University of Technology.

[‡] Northwestern University.

(1) (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113–117. (b) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–188.

(2) (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139–144. (b) Carty, A. *Organomet. Chem. Rev., Sect. A* **1972**, *7*, 191–243.

0002-7863/81/1503-3014$01.25/0