

reflections accessible for ψ scans with the helium tunnel in place, and the crystal did not have sufficiently well defined faces for indexing for a numerical correction. The positions and anisotropic displacement parameters for the Br and Cl atoms at each site were constrained to be the same. H atoms were included in calculated positions using the riding model, with displacement parameters 1.2 times U_{eq} of the atoms to which they were bonded. The largest peaks on the final difference map were close to the Re atom.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1176). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Bombieri, G., Benetollo, F., Bagnall, K. W., Plews, M. J. & Brown, D. (1983). *J. Chem. Soc. Dalton Trans.* pp. 343–348.
- Chat, J. & Rowe, G. A. (1962). *Inorg. Chem.* **1**, 4019–4033.
- Ciana, G., Sironi, A., Beringhelli, T., Alfonso, G. D. & Freni, M. (1986). *Inorg. Chim. Acta*, **113**, 61–65.
- Felcman, J., Cândida, M., Vaz, T. A. & Fraústo da Silva, J. J. R. (1984). *Inorg. Chim. Acta*, **93**, 101–108.
- Harben, S. M., Smith, P. D., Beddoes, R. L., Collison, D. & Garner, C. D. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2777–2784.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Mronga, N., Weller, F. & Dehnicke, K. (1983). *Z. Anorg. Allg. Chem.* **502**, 35–44.
- Roncari, E., Mazzi, U., Rossi, R., Duatti, A. & Magon, L. (1981). *Transition Met. Chem.* **6**, 169–173.
- Rossi, R., Marchi, A., Marvelli, L., Magon, L., Peruzzini, M., Casellato, U. & Graziani, R. (1993). *Inorg. Chim. Acta*, **204**, 63–71.
- Rossi, R., Marvelli, L., Marchi, A., Magon, L., Bertolasi, V. & Ferretti, V. (1994). *J. Chem. Soc. Dalton Trans.* pp. 339–345.
- Sergienko, V. S., Porai-Koshits, M. A., Mistryukov, V. E. & Kotegov, K. V. (1982). *Sov. J. Koord. Khim.* **8**, 119–124.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Szymańska-Buzar, T. & Glowiak, T. (1995). *J. Organomet. Chem.* **490**, 203–207.
- Tudela, D., Tomero, J. D., Monge, A. & Sanchez-Hereñcia, A. J. (1993). *Inorg. Chem.* **32**, 3928–3930.
- Tursina, A. I., Yatsenko, A. V., Medvedev, S. V., Chernyshev, V. V. & Aslanov, L. A. (1986). *Zh. Strukt. Khim.* **27**, 155–157.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

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Hexacarbonyl-1 κ^3 C,2 κ^3 C-bis{1,2(η^5)-1-[2-(trimethylsiloxy)ethyl]cyclopentadienyl}dimolybdenum(Mo—Mo)

KATHARINE J. COVERT, JONATHAN L. MALE, DAVID R. TYLER AND TIMOTHY J. R. WEAKLEY

Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, USA. E-mail: tweakley@oregon.uoregon.edu

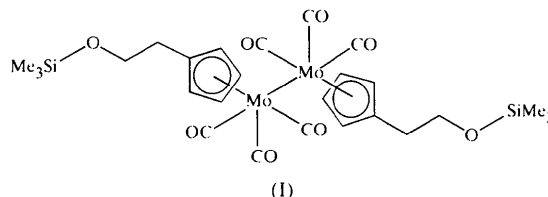
(Received 22 October 1997; accepted 12 January 1998)

Abstract

The title complex molecule, $[\text{Mo}_2(\text{C}_{10}\text{H}_{17}\text{OSi})_2(\text{CO})_6]$, lies on a crystallographic inversion center. Each Mo atom exhibits ‘four-legged piano-stool’ bond geometry, with the other Mo atom at a basal position $[\text{Mo}—\text{Mo}$ 3.219 (1) Å].

Comment

We have shown (Covert *et al.*, 1992) that the cage effect for the photogenerated radical pair $[(\text{MeCp})(\text{CO})_3\text{Mo}, \text{Mo}(\text{CO})_3(\text{MeCp})]$ is smaller than for the heavier tungsten analogue (MeCp is methylcyclopentadienyl). In order to separate changes due to difference in radical mass from changes due to bond energies or spin-orbit coupling, we have synthesized and studied the title molecule, $(\text{CpCH}_2\text{CH}_2\text{OSiMe}_3)_2\text{Mo}_2(\text{CO})_6$, (I). This molecule has a similar mass to $(\text{MeCp})_2\text{W}_2(\text{CO})_6$. The $-\text{CH}_2\text{CH}_2-$ spacer insulates the Cp ring from substituent electronic effects. A comparison of the cage effects for the three molecules has allowed us to consider the influence of different $M—M$ bond energies.



The molecule lies on a crystallographic inversion center. The side chain in each moiety is directed away from the $\text{Mo}_2(\text{CO})_6$ region in such a way that one

methyl group (C11) is 3.456(8) Å above the Cp ring in a direction 5.1(4)° from the normal to the ring at the centroid. The 'four-legged piano-stool' bond geometry about molybdenum, with the second Mo atom at one basal position, is identical to that in the synthetic precursor (CpCH₂CH₂OH)₂Mo₂(CO)₆ (Tenhaeff *et al.*, 1991) and in (MeCp)₂Mo₂(CO)₆ (Tyler & Weakley, 1995). Corresponding bond lengths and angles in these three molecules are very similar. In particular, the Mo—Mo bond lengths in the title molecule [3.219(1) Å] and in (MeCp)₂Mo₂(CO)₆ [3.220(1) Å] are identical, and so are the energies of the electronic absorption bands assigned to the Mo—Mo σ—σ* transitions. As discussed by Lindfors *et al.* (1997), these features suggest that the Mo—Mo bond is not significantly perturbed by the change in the side chain and that therefore the Mo—Mo bond energies are essentially the same.

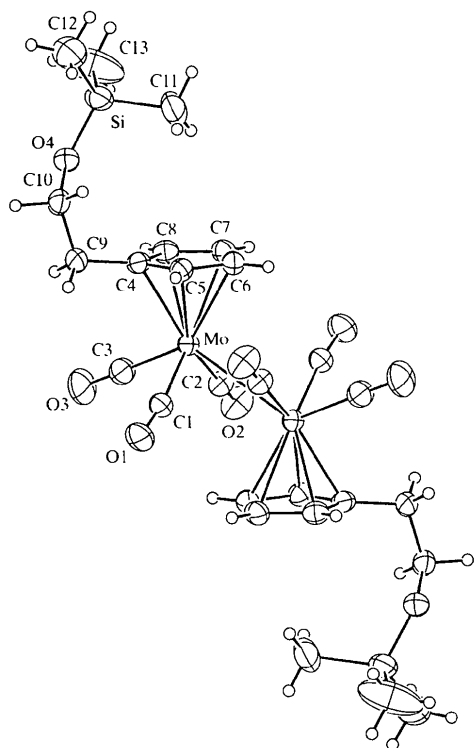


Fig. 1. The molecular structure of (η⁵-Me₃SiOCH₂CH₂C₅H₄)₂Mo₂(CO)₆ (30% probability ellipsoids).

Experimental

The title complex was synthesized according to Lindfors *et al.* (1997). The data crystal (recrystallized from hexane) was cleaved under hydrocarbon grease and sealed in a capillary.

Crystal data

[Mo₂(C₁₀H₁₇OSi)₂(CO)₆]
M_r = 722.60

Mo Kα radiation
λ = 0.71073 Å

Triclinic
P $\bar{1}$
a = 7.863(3) Å
b = 8.171(2) Å
c = 13.415(3) Å
α = 78.11(2)°
β = 74.40(3)°
γ = 85.12(3)°
V = 812.0(9) Å³
Z = 1
D_c = 1.478 Mg m⁻³
D_m not measured

Data collection

Enraf-Nonius CAD-4
diffractometer
ω/2θ scans
Absorption correction:
ψ scan (North *et al.*,
1968)
T_{min} = 0.836, T_{max} = 0.933
3080 measured reflections
2849 independent reflections

Refinement

Refinement on F
R = 0.031
wR = 0.033
S = 1.48
2410 reflections
204 parameters
H atoms treated by a
mixture of independent
and constrained refinement

Cell parameters from 25
reflections
θ = 12–14°
μ = 0.865 mm⁻¹
T = 294 K
Tablet
0.29 × 0.25 × 0.08 mm
Red

2410 reflections with
I > σ(I)
R_{int} = 0.022
θ_{max} = 25.0°
h = 0 → 9
k = -9 → 9
l = -14 → 15
3 standard reflections
frequency: 60 min
intensity decay: 11.5%

w = 4F_o²/[σ²(I) + (0.02I)²]
(Δ/σ)_{max} = 0.036
Δρ_{max} = 0.53 e Å⁻³
Δρ_{min} = -0.48 e Å⁻³
Extinction correction: none
Scattering factors from
Cromer & Waber (1974)

Table 1. Selected geometric parameters (Å, °)

Mo—Mo ¹	3.219(1)	O1—C1	1.152(5)
Mo—C1	1.969(4)	O2—C2	1.143(4)
Mo—C2	1.979(4)	O3—C3	1.161(5)
Mo—C3	1.932(4)	O4—C10	1.419(5)
Mo—C4	2.320(4)	C4—C5	1.407(5)
Mo—C5	2.340(4)	C4—C8	1.419(5)
Mo—C6	2.364(4)	C5—C6	1.407(5)
Mo—C7	2.348(4)	C6—C7	1.384(6)
Mo—C8	2.306(4)	C7—C8	1.407(6)
Si—O4	1.632(3)		
C1—Mo—C2	106.7(2)	O4—Si—C13	103.3(3)
C1—Mo—C3	78.0(2)	Si—O4—C10	126.0(3)
C2—Mo—C3	78.0(2)	Mo—C1—O1	172.8(4)
O4—Si—C11	111.3(2)	Mo—C2—O2	174.3(4)
O4—Si—C12	112.6(2)	Mo—C3—O3	179.0(4)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

The data were corrected for decay and for absorption (North *et al.*, 1968). The Mo atom was located from the Patterson map. The methyl groups showed considerable apparent thermal motion, but there were no clear indications of alternative partially occupied positions. H atoms were located and refined, except for those of methyl groups, which were included at calculated positions [C—H 0.95 Å and U(H) = 1.2U₃₃(C)]. The value of a secondary extinction parameter (Stout & Jensen, 1968) was predicted to be negative and was fixed at zero.

Data collection: CAD-4/PC Software (Enraf-Nonius, 1993). Cell refinement: CAD-4/PC Software. Data reduction:

TEXSAN (Molecular Structure Corporation, 1989). Program(s) used to solve structure: TEXSAN. Program(s) used to refine structure: TEXSAN. Software used to prepare material for publication: TEXSAN.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1100). Services for accessing these data are described at the back of the journal.

References

- Covert, K. J., Askew, E. F., Grunkemeier, J., Koenig, T. & Tyler, D. R. (1992). *J. Am. Chem. Soc.* **114**, 10446–10448.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 77, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Enraf-Nonius (1993). *CAD-4/PC Software*. Version 1.2. Enraf-Nonius, Delft, The Netherlands.
- Lindfors, B. E., Male, J. L., Covert, K. J. & Tyler, D. R. (1997). *Chem. Commun.* pp. 1687–1688.
- Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination: A Practical Guide*, p. 411. London: Macmillan Co.
- Tenhaeff, S. C., Tyler, D. R. & Weakley, T. J. R. (1991). *Acta Cryst.* **C47**, 303–305.
- Tyler, D. R. & Weakley, T. J. R. (1995). Unpublished results.

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(Benzenethiolato-*S*)(4-*tert*-butylpyridine-*N*)bis(dimethylglyoximato-*N,N'*)cobalt(III) and (4-*tert*-Butylpyridine-*N*)bis(dimethylglyoximato-*N,N'*)(4-methoxybenzenethiolato-*S*)cobalt(III)

YOSHINOBU INOUE,^a TOHRU KAMBE^b AND MASARU TADA^{a,b}

^aDepartment of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan, and ^bDepartment of Chemistry, School of Science and Engineering, Waseda University, Shinjuku, Tokyo 169, Japan. E-mail: inouye@staff.chem.tsukuba.ac.jp

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Abstract

The Co—S distances in the title compounds, [Co(C₄H₇N₂O₂)₂(C₉H₁₃N)(C₆H₅S)] and [Co(C₄H₇N₂O₂)₂(C₉H₁₃N)(C₇H₇OS)], are 2.2800 (8) and 2.2885 (15) Å,

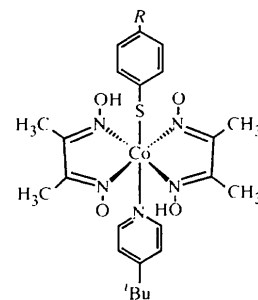
respectively. The electron-donating substituent on the *para* position of the arylthiolate lengthens the Co—S bond.

Comment

A Co—S coordination is one of the possible models of coenzyme B₁₂ involvement in biological methyl transfer from a tetrahydrofolate coenzyme to homosystemin, which is mediated by coenzyme B₁₂ (Matthews, 1984; Taylor, 1982). Model studies using cobaloxime, Co(DH)₂, as a coenzyme B₁₂ model showed that a variety of reaction schemes are envisaged for the reaction of the cobalt complex and thiol (Schrauzer & Windgassen, 1967; Jacobsen *et al.*, 1993; Polson *et al.*, 1997). Although the crystal structures of cobaloxime derivatives, Co(DH)₂L¹L², have been widely investigated and reviewed (Pahor *et al.*, 1985; Randaccio *et al.*, 1989), only a few compounds involving sulfur ligands have been reported (L¹ and/or L² = SR; Polson *et al.*, 1997, and references therein).

As a model reaction of biological methyl transfer from methyltetrahydrofolic acid to coenzyme M, we studied the methyl transfer from the N5-methyltetrahydropteridinium ion to arylthiocobaloxime. The reaction simulated the methyl transfer from the ammonium ion to the arylthio group to give methyl aryl sulfide, and the relative reactivity of the arylthiocobaloximes decreased in the order *p*-methoxyphenylthio-, phenylthio-, *p*-chlorophenylthio- and *p*-cyanophenylthiocobaloxime (Tada *et al.*, 1998).

If the alkyl transfer starts by the initial homolysis of the Co—S bond, the reactivity must follow the bond strength and hence the bond distance of the Co—S bond. The crystal structures of [Co(DH)₂(4-*t*-BuPy)(PhS)], (1), and [Co(DH)₂(4-*t*-BuPy)(4-MeO-PhS)], (2), were investigated on this premise.



- (1) R = H
(2) R = OCH₃

The geometries around the cobaloxime moiety [Co(DH)₂] are normal in both crystals. The deviation of cobalt from the best plane of the four equatorial N atoms (N1–N4) is 0.050 (1) and 0.059 (2) Å in (1) and (2), respectively, while the twisting of the two DH