Available online at www.sciencedirect.com

ScienceDirect

Polyhedron 25 (2006) 3413–3416

POLYHEDRON

www.elsevier.com/locate/poly

Molybdenum S-bonded mono-thiocarboxylate complexes $CpMo(CO)_3SCOR$: Structure of $CpMo(CO)_3SCOPh$

Mohammad El-khateeb [a,*], Tobias Rüffer [b], Heinrich Lang [b]

[a] *Chemistry Department, Jordan University of Science and Technology, Irbid 22110, Jordan*
[b] *Institut für Chemie, Technische Universität Chemnitz, Strasse der Nationen 62, Chemnitz D-09107, Germany*

Received 12 March 2006; accepted 13 June 2006
Available online 3 July 2006

Abstract

Monothiocarboxylate complexes of molybdenum of the type $CpMo(CO)_3SCOR$ [R = Me (**1**), CH_2Cl (**2**), Ph (**3**), 4-$C_6H_4NO_2$ (**4**), 3,5-$C_6H_3(NO_2)_2$ (**5**)] have been obtained by the reaction of the hydrosulfido complex, $CpMo(CO)_3SH$, with acid chlorides. Complexes **1**–**5** have been characterized by IR and ^{1}H-NMR spectroscopy, elemental analyses and by the single crystal X-ray diffraction of **3**.

Keywords: Molybdenum; Cyclopentadienyl; X-ray structure; Thiocarboxylate; Sulfur; Carbonyl

1. Introduction

Transition metal chalcogeno complexes have attracted considerable attention due to their structural diversity [1–6], relevance to catalysis [7–12] and biological applications as models for metalloenzymes [13–16]. An interesting class of metal–chalcogeno complexes is that containing thiocarboxylate ligands, which have been known for a long time [17–29]. They have been prepared by two main routes: the first one includes the substitution of an uninegative labile ligand on the transition metal by thiocarboxylate anions [20,21], while the second method is represented by modifying a sulfur-containing metal complex featuring sulfides (S_x^{2-}) or hydrosulfido (SH^-) ligands [17–19,26].

The first route has been applicable for a wide range of metal–thiocarboxylate complexes. For example, the salts, $Ph_4P[M(SCOPh)_2]$ (M = Cu, Ag) and $Et_3HN[Ag(SCOPh)_2]$ were synthesized from the appropriate metal salts and the benzoyl thiocarboxylate anion, $PhCOS^-$ [16]. The palladium thioacetate complexes $P_2Pd(SCOMe)_2$ (P = PPh_3, 1/2 dppf) were also made by the reaction of P_2PdCl_2 with the thioacetate anion [17]. The Cp-free complexes $Mo(CO)_2(PPh_3)_2Br(SCOR)$ have been prepared from the reaction of $Mo(CO)_2(PPh_3)_2Br_2$ with thiocarboxylate anions [20].

As far as the second route is concerned, the reaction of the iron sulfides (μ-S_x)$[CpFe(CO)_2]_2$ ($x = 2, 3$), with acid chlorides has been reported to give the thiocarboxylate complexes, $CpFe(CO)_2SCOR$ [22,23]. This chemistry was also extended to include the Cp-substituted species $Cp'Fe(CO)_2SCOR$ ($Cp' = C_5H_4Bu^t$, 1,3-$C_5H_3(Bu^t)_2$; R = alkyl, aryl) [24]. The photolytic reaction of these thiocarboxylate complexes with EPh_3 (E = P, As, Sb) produced the substituted complexes $Cp'Fe(CO)(EPh_3)SCOR$ [30]. An extension of this approach to include the reaction of the ruthenium sulfide (μ-S_5)$[CpRu(CO)_2]_2$ with acid chlorides to give the ruthenium thiocarboxylate complexes $CpRu(CO)_2SCOR$ has been reported [25]. However, the mixed phosphine–carbonyl ruthenium complexes $CpRu(CO)(PPh_3)SCOR$ were prepared from the reaction of $CpRu(CO)(PPh_3)SH$ with acid chlorides at low temperature [26]. The later reaction was also applied successfully to the preparation of $CpRu(L)(L')SCOR$ ($L = L' = PPh_3$, $1/2Ph_2PCH_2PPh_2$, $1/2Ph_2PCH_2CH_2PPh_2$) [26].

The importance of Mo–thiocarboxylate complexes in biochemistry [31,32] prompted us to extend our studies on the synthesis and characterization of metal thiocarboxylate

---

[*] Corresponding author. Tel.: +962 2 7201000; fax: +962 2 7095014.
E-mail address: kateeb@just.edu.jo (M. El-khateeb).

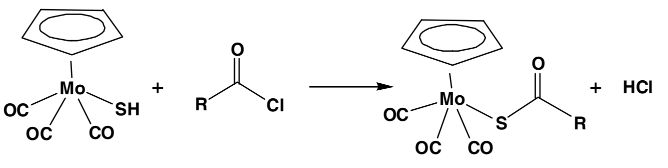
0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.06.021

complexes to include molybdenum. The reaction between CpMo(CO)$_3$SH and acid chlorides which gives the expected thiocarboxylate complexes CpMo(CO)$_3$SCOR is discussed in this report.

2. Results and discussion

2.1. Synthesis and characterization

Treatment of the molybdenum hydrosulfido complex CpMo(CO)$_3$SH with acid chlorides gave the thiocarboxylate complexes CpMo(CO)$_3$SCOR, **1**–**5** as shown in the following equation:



1 - 5

R= Me (**1**), CH$_2$Cl (**2**), Ph (**3**), 4-C$_6$H$_4$NO$_2$ (**4**), 3,5-C$_6$H$_3$(NO$_2$)$_2$ (**5**)

(1)

The resulting dark-red thiocarboxylate complexes, **1**–**5**, are air stable as solids. In solution, these complexes are quite unstable and they decompose to brown insoluble materials. In some experiments small amounts of the chloride complex CpMo(CO)$_3$Cl were also obtained. Complexes **1**–**5** have been fully characterized by IR, ^{1}H NMR spectra, elemental analysis and by the single crystal X-ray structure determination of **3**. The IR spectra of **1**–**5** display three absorption bands in the range of 2048–2042, 1980–1971, and 1936–1942 cm^{-1}, respectively, for the terminal carbonyl ligands. These bands are lower than those observed for CpMo(CO)$_3$SH (2039, 1963 cm^{-1}) [33,34], but similar to those observed for CpMo(CO)$_3$S$_2$CSR (2050–2046, 1976, and 1951–1952 cm^{-1}) [35]. An additional distinctive absorption appears between 1644 and 1736 cm^{-1}, corresponding to the ketonic carbonyl group of the thiocarboxylate ligand. This value is higher than those observed for the analogous iron thiocarboxylates CpFe(CO)$_2$SCOR (1590–1630 cm^{-1}), suggesting less electron density around the Mo center compared to that of Fe.

The ^{1}H NMR spectra of **1**–**5** show the expected signals of the Cp protons in the range 5.55–5.66 ppm. These resonances are found at lower field than the peak for CpMo(CO)$_3$SH (4.55 ppm) and CpMo(CO)$_3$(S$_2$CSR) (4.32 ppm), suggesting that the thiocarboxylate group is a stronger π-acceptor (or weaker σ-donor) ligand compared to the thioxanthate unit [35]. The peaks for the R-group of the thiocarboxylate ligands are shown in the expected ranges with the expected multiplicities.

2.2. Crystal structure

The molecular structure of **3** with the atom numbering scheme is shown in Fig. 1. Selected bond distances (Å) and angles (°) of **3** are presented in Table 1. The crystal lattice of **3** contains two crystallographically independent molecules. The Cp-ring is bonded to the molybdenum atom in a η^5-fashion with Mo–C bond distances ranging from 2.295(4) Å to 2.355(4) Å. The Mo–S bond distance 2.5191(10) Å is similar to that reported for Mo(κ^2C,S-SCOPr^i)(κS-SCOMe)(CO)$_2$(PMe$_3$)$_2$, 2.511(4) Å [28]. The Mo–C$_{\mathrm{CO}}$ bond distances (average of 1.986 Å) are in agreement with those found in CpMo(CO)$_3$-containing complexes. The C=O bond distance of the thiocarboxylate ligand of 1.214(5) Å is similar to that reported for Mo(κ^2C,S-SCOPr^i)(κS-SCOMe)(CO)$_2$(PMe$_3$)$_2$ of 1.19(2) Å [28] and to that found in other complexes containing thiocarboxylate groups [22,26].

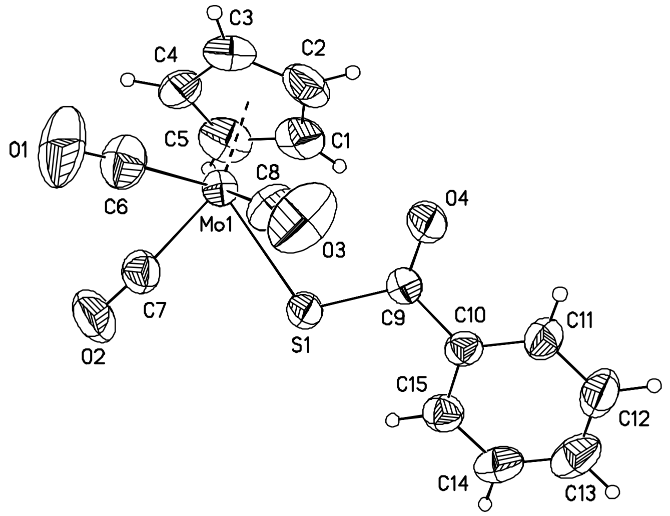


Fig. 1. ORTEP drawing of CpMo(CO)$_3$SCOC$_6$H$_5$ (**3**).

Table 1
Selected bond lengths (Å) and angles (°) of CpMo(CO)$_3$SCOC$_6$H$_5$ (**3**)

Mo1–S1	2.5191(10)
Mo1–C1	2.355(4)
Mo1–C2	2.345(4)
Mo1–C3	2.304(4)
Mo1–C4	2.295(4)
Mo1–C5	2.312(4)
Mo1–C6	1.973(5)
Mo1–C7	1.989(4)
Mo1–C8	1.995(4)
S1–C9	1.753(3)
C9–O4	1.214(5)
C6–O1	1.153(5)
C7–O2	1.143(5)
C8–O3	1.128(5)
C6–Mo1–C7	76.71(17)
C7–Mo1–C8	77.96(17)
C6–Mo1–C8	111.39(18)
C6–Mo1–S1	133.10(14)
C7–Mo1–S1	76.57(12)
C8–Mo1–S1	76.93(11)
Mo1–S1–C9	107.45(12)
O4–C9–S1	123.8(3)

3. Experimental

3.1. General

Synthetic work was carried out under a dinitrogen atmosphere using Schlenk techniques. Tetrahydrofuran, diethyl ether, hexane, and dichloromethane were dried, distilled and stored under nitrogen. The reagent $CpMo(CO)_3SH$ was prepared as described previously [34,35]. Acid chlorides, molybdenum hexacarbonyl and sulfur were obtained commercially and were used as received.

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker spectrometer operating at 200 MHz with chemical shifts reported in ppm downfield from TMS, using the solvent residual peak as an internal reference. Infrared (IR) spectra were recorded on a Nicolet-Impact 410 FT-IR spectrometer in CH_2Cl_2 solutions. Elemental analyses were done at Laboratoire D'Analyse Élementaire, Universite de Montréal, Montréal, Québec, Canada. Melting points were reported on a Staurt Melting point apparatus (SMP3) and are uncorrected.

*3.2. General procedure for the preparation of $CpMo(CO)_3SCOR$, **1–5***

A diethyl ether solution of $CpMo(CO)_3SH$ (0.28 g, 1.00 mmol) was cooled to −78 °C. The respective acid chloride (1.10 mmol) was added as one portion. The cooling bath was removed and the solution was stirred for 2 h at room temperature. The volatiles were removed under vacuum and the resulting solid was redissolved in a minimum amount of dichloromethane and introduced onto a silica gel column made up with hexane. Elution with hexane removes the excess acid chlorides and with a 1:1 v:v ratio of diethyl ether:hexane gives an orange band. This band was collected and the volatiles were removed under vacuum. The resulting red solid was recrystallized from dichloromethane/hexane at 0 °C.

*3.2.1. $CpMo(CO)_3SCOMe$ (**1**)*

Yield: 70%. M.p.: 193–194 °C. IR (CH_2Cl_2, cm^{-1}): 2044 (s), 1971 (s), 1936 (s) ($\nu(C\equiv O)$), 1644 (m) ($\nu(C=O)$). ^1H-NMR ($CDCl_3$): δ 2.49 (s, 3H, CH_3), 5.55 (s, 5H, C_5H_5). *Anal.* Calc. for $C_{10}H_8MoO_4S$: C, 37.51; H, 2.52; S, 10.01. Found: C, 37.08; H, 2.32; S, 9.74%.

*3.2.2. $CpMo(CO)_3SCOCH_2Cl$ (**2**)*

Yield: 75%. M.p.: 150–151 °C. IR (CH_2Cl_2, cm^{-1}): 2048 (s), 1980 (s), 1957 ($\nu(C\equiv O)$), 1736 (m) ($\nu(C=O)$). ^1H-NMR ($CDCl_3$): δ 4.15 (s, 2H, CH_2Cl), 5.59 (s, 5H, C_5H_5). *Anal.* Calc. for $C_{10}H_7ClMoO_4S$: C, 33.87; H, 1.99; S, 9.04. Found: C, 33.17; H, 1.89; S, 8.33%.

*3.2.3. $CpMo(CO)_3SCOPh$ (**3**)*

Yield: 65%. M.p.: 108–110 °C. IR (CH_2Cl_2, cm^{-1}): 2042 (s), 1976 (s), 1941 (s) ($\nu(C\equiv O)$), 1685 (m) ($\nu(C=O)$). ^1H-NMR ($CDCl_3$): 5.63 (s, 5H, C_5H_5), 7.40 (m, 3H, C_6H_5), 8.30 (m, 2H, C_6H_5). *Anal.* Calc. for $C_{15}H_{10}MoO_4S$: C, 47.13; H, 2.64; S, 8.39. Found: C, 46.83; H, 2.28; S, 7.98%.

*3.2.4. $CpMo(CO)_3SCO\text{-}4\text{-}C_6H_4NO_2$ (**4**)*

Yield: 87%. M.p.: 134–135 °C. IR (CH_2Cl_2, cm^{-1}): 2045 (s), 1977 (s), 1942 (s) ($\nu(C\equiv O)$), 1707 (m) ($\nu(C=O)$). ^1H-NMR ($CDCl_3$): 5.64 (s, 5H, C_5H_5), 8.32 (2d, 4H, $C_6H_4NO_2$, $J_o = 9.1$ Hz). *Anal.* Calc. for $C_{15}H_9MoNO_6S$: C, 42.17; H, 2.12; N, 3.29; S, 7.50. Found: C, 41.86; H, 1.87; N, 2.95; S, 7.02%.

*3.2.5. $CpMo(CO)_3SCO\text{-}4\text{-}C_6H_3(NO_2)_2$ (**5**)*

Yield: 87%. M.p.: 162–163 °C. IR (CH_2Cl_2, cm^{-1}): 2046 (s), 1977 (s), 1941 (s) ($\nu(C\equiv O)$), 1710 (m) ($\nu(C=O)$). ^1H-NMR ($CDCl_3$): 5.66 (s, 5H, C_5H_5), 8.33 (d, 2H, $C_6H_3(NO_2)_2$, $J_m = 3.1$ Hz), 8.67 (t, 1H, $C_6H_3(NO_2)_2$, $J_m = 3.1$ Hz). *Anal.* Calc. for $C_{15}H_9MoN_2O_8S$: C, 38.23; H, 1.50; N, 5.94; S, 6.80. Found: C, 37.75; H, 1.37; N, 5.45; S, 6.38%.

3.3. X-ray structure analysis

X-ray data of a dark red crystal of $CpMo(CO)_3SCOPh$ (**3**) were collected with an Oxford Gemini S diffractomer with a graphite monochromator $\lambda(\text{Mo K}\alpha) = 0.71073$ Å. The crystallographic data are presented in Table 2. The structure was solved by direct methods using SHELXS-97 [36] and refined by full-matrix least-square procedures on

Table 2
Selected crystal data and refinement parameters for $CpMo(CO)_3SCOC_6H_5$ (**3**)

Empirical formula	$C_{15}H_{10}MoO_4S$
Formula weight	382.23
Crystal size (mm)	0.3 × 0.3 × 0.2
Crystal system	Orthorhombic
Space group	*Pca2(1)*
Unit cell dimension	
a (Å)	33.833 (3)
b (Å)	7.6070 (5)
c (Å)	11.7042 (9)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3012.3 (4)
Z	8
Index ranges	$-40 \leqslant h \leqslant 40$
	$-9 \leqslant k \leqslant 9$
	$-13 \leqslant l \leqslant 14$
Refections collected/unique [R_{int}]	19510/5385 [0.0321]
Data/restrains/parameters	5385/1/379
GooF	1.062
D_{calc} (Mg m^{-3})	1.686
μ (mm^{-1})	1.020
θ Range (°)	2.94–25.20
$R[F^2 > 2\sigma(F^2)]$	0.0279
$\omega R(F^2)$[a]	0.0501
Flack x parameter[b]	0.02(3)

[a] $\omega = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 1.5711P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[b] H.D. Flack, Acta Crystallogr., Sect. A (39) (1983) 876.

F^2, using SHELXTL-97 [37]. All non-hydrogen atoms are refined anisotropically and the hydrogen atom positions have been refined using the riding model. The absolute structure was determined by the refinement of the Flack x parameter. The asymmetric unit comprises two independent molecules.

Acknowledgements

The authors thank the Deanship of Research, Jordan University of Science and Technology and Shoman Foundation for financial support.

Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 600973 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.06.021.

References

[1] H.J. Gysling, Coord. Chem. Rev. 42 (1982) 133.

[2] P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121.

[3] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgren, J. Organomet. Chem. 587 (1999) 200.

[4] I.G. Dance, Polyhedron 5 (1986) 1037.

[5] V.G. Albano, M. Monari, I. Orabona, A. Panunzi, G. Roviello, F. Rufo, Organometallics 22 (2003) 1223.

[6] A.J. Canty, M.C. Denney, J. Patel, H. Sun, B.W. Skelton, A.H. White, J. Organomet. Chem. 689 (2004) 672.

[7] C.N. Satterfield, in: Heterogeneous Catalysis in Industrial Practice, 2nd ed., McGraw-Hill, New York, 1991, pp. 378–384.

[8] J.R. Dilworth, N. Wheatley, Coord. Chem. Rev. 199 (2000) 89.

[9] D.V. Vivic, W.D. Jones, Organometallics 18 (1999) 134.

[10] A. Shaver, H. Boily, A.-M. Lebuis, Inorg. Chem. 35 (1996) 6356.

[11] A. Shaver, M. El-khateeb, A.-M. Lebuis, Angew. Chem., Int. Ed. Engl. 35 (1996) 2362.

[12] S. Dey, V.K. Jain, S. Chaudhury, A. Knoedler, F. Lissner, W. Kaim, J. Chem. Soc., Dalton Trans. (2001) 723.

[13] Q. Liu, J. Lin, P. Jiang, J. Zhang, L. Zhu, Z. Guo, Eur. J. Inorg. Chem. (2002) 2170.

[14] E.R. Jamieson, S.J. Lippard, Chem. Rev. 99 (1999) 2467.

[15] K.M. Williams, C. Rowan, J. Mitchell, Inorg. Chem. 43 (2004) 1190.

[16] J.T. Saponthar, J.J. Vittal, P.A.W. Dean, J. Chem. Soc., Dalton Trans. (1999) 3135.

[17] Y.C. Neo, J.J. Vittal, T.S.A. Hor, J. Organomet. Chem. 637–639 (2001) 575.

[18] J.M. Lisy, E.D. Dobrzynski, R.J. Angelici, J. Clardy, J. Am. Chem. Soc. 97 (1975) 656.

[19] T.C. Deivaraj, G.X. Lai, J.J. Vittal, Inorg. Chem. 39 (2000) 1028.

[20] V. Riera, F.J. Arnaiz, G.G. Herbosa, J. Organomet. Chem. 315 (1986) 51.

[21] F.A. Cotton, P.E. Fanwick, R.H. Niswander, J.C. Sekutowski, Acta Chem. Scan. A 32A (1978) 663.

[22] M.A. El-Hinnawi, A. Ajlouni, J. Abu-Nasser, K. Powell, H. Vahrenkamp, J. Organomet. Chem. 359 (1989) 79.

[23] M.A. El-Hinnawi, A. Ajlouni, J. Organomet. Chem. 332 (1987) 321.

[24] M.A. El-Hinnawi, M. El-khateeb, I. Jibril, S.T. Abu-Orabi, Synth. React. Inorg. Met. Org. Chem. 19 (1989) 309.

[25] M.A. El-Hinnawi, F.T. Smadi, M. Esmadi, J. Organomet. Chem. 377 (1989) 373.

[26] W.A. Schenk, N. Sonnhalter, N. Burzlaff, Z. Naturforsch. 52b (1997) 117.

[27] R. Devy, J.J. Vittal, Inorg. Chem. 37 (1998) 6939.

[28] L. Contreras, F.R. Lainez, A. Pizzano, L. Sanchez, E. Carmona, A. Monge, C. Ruiz, Organometallics 19 (2000) 261.

[29] M. Cindric, D. Matkovic-Calogovic, V. Vrdoljak, B. Kamenar, Inorg. Chim. Acta 284 (1999) 223.

[30] I. Jibril, M.A. El-Hinnawi, M. El-khateeb, Polyhedron 10 (1991) 2095.

[31] A. Matthies, K.V. Rajagopalan, R.R. Mendel, S. Leimkuehler, Proc. Natl. Acad. Sci. USA 101 (2004) 5946.

[32] M.M. Wuebbens, K.V. Rajagopalan, J. Biol. Chem. 278 (2003) 14523.

[33] U. Behrens, F. Edelmann, J. Organomet. Chem. 263 (1984) 179.

[34] A. Bauer, K.B. Capps, B. Wixmerten, K.A. Abboud, C.D. Hoff, Inorg. Chem. 28 (1999) 2136.

[35] W. Dean, B. Heyl, J. Organomet. Chem. 159 (1978) 171.

[36] G.M. Sheldrick, Acta Crystallogr., Sec. A: Fund. Crystallogr. 46 (1990) 467.

[37] G.M. Sheldrick, SHELXS-97 (Release 97-2), University of Göttingen, Germany, 1997.