Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(η^5-Cyclopentadienyl)(*N*,*N*-dimethyldithiocarbamato-$\kappa^2 S,S'$)[η^4-tetrakis(trifluoromethyl)cyclobutadienyl]molybdenum(IV)

Jack L. Davidson,[a] Alice Jarvie[b] and Kenneth W. Muir[b]*

[a]School of Engineering and Physical Sciences, Heriot–Watt University, Edinburgh EH14 4AS, Scotland, and [b]Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland
Correspondence e-mail: ken@chem.gla.ac.uk

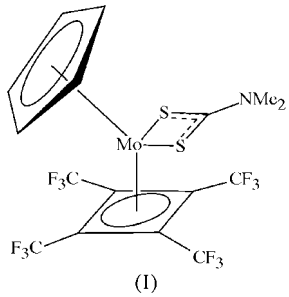
Received 23 February 2005
Accepted 24 February 2005
Online 25 March 2005

The title complex, $[Mo(C_8F_{12})(C_5H_5)(C_3H_6NS_2)]$, contains both a η^4-$C_4(CF_3)_4$ cyclobutadienyl ligand with approximate C_{4v} local symmetry and a η^5-C_5H_5 cyclopentadienyl ring. The centroids of the rings and the S atoms of a chelating dithiocarbamate ligand define the pseudo-tetrahedral coordination of the Mo atom. The Mo—C(cyclobutadienyl) bond lengths [2.189 (2)–2.211 (2) Å] are unusually short, probably reflecting strong electron withdrawal by the trifluoromethyl groups. The molecules straddle crystallographic mirror planes.

Comment

Complexes with η^4-C_4R_4 cyclobutadienyl ligands are known for many transition metals. For example, nine structures containing the (η^4-C_4R_4)Mo moiety occur in the Cambridge Structural Database (CSD; Version 5.25 of November 2003; Allen, 2002) (structural searches were carried out locally using the *QUEST* and *CONQUEST* search programs). In most of these compounds, R = Ph (CSD refcodes GICGUU10, LUJZOF, LUKBAU, LUJZUL, PABPMO, PCBMOC10 and TPCBMO), but an R = p-$CH_3C_6H_4$ complex (GIQTIJ) and a C_4Ph_3Me species (COXVIU) have also been characterized (see supplementary data for a list of references). We now describe the structure of the title compound, CpCbMo(S_2CNMe_2), (I), where Cp = η^5-C_5H_5 and Cb = η^4-$C_4(CF_3)_4$. Compound (I) is the first structural example of a η^4-$C_4(CF_3)_4$ complex of any transition metal.

Molecules of (I) have exact C_s symmetry; atoms Mo1, N1, C1, C3, C8–C11, F4 and F7 all lie on a crystallographic mirror plane in space group $P2_1m$ (Fig. 1). The metal coordination is pseudo-tetrahedral, being defined by *Cp*—Mo—*Cb* and S—Mo—S^i angles of 136.6 (2) and 70.0 (1)° (here *Cp* and *Cb* are the centroids of the C_5 and C_4 rings; symmetry code as in Table 1). The bonding in pseudo-tetrahedral CpCbMoL_2 species such as (I) has been reviewed by Curnow *et al.* (1993), who argue that the Cb ligand is best considered as a dianionic $C_4R_4^{2-}$ six-electron donor isoelectronic with Cp^-, making (I) a d^2 Mo^{IV} complex. The metal lone pair in such complexes occupies a stereochemically active d_{z^2}-like orbital, compressing the L—M—L angle. Thus, the Cl—Mo—Cl angle in Cp_2MoCl_2 (Prout *et al.*, 1974) is 82°, only 12° less acute than the S—Mo—S^i angle in (I).



(I)

The Mo—S distance in (I) (Table 1) differs by only 0.002 (1) Å from the comparable mean of 2.472 Å in the isoelectronic Mo^{IV} cation $[Mo(\eta^5\text{-In})_2(S_2CNEt_2)]^+$ (In is indenyl; Drew *et al.*, 1998). The Mo—C(Cp) bond lengths are also unexceptional and the displacement of the Mo atom from the Cp plane [2.012 (1) Å] is close to the average of 2.008 (1) Å for all CpMo compounds in the CSD. However, (i) variations in Cp ring C—C distances and angles [1.338 (9)–1.391 (4) Å and 105.9 (4)–109.2 (2)°] and (ii) U_{eq} values of Cp ring C atoms nearly three times that of the Mo atom both suggest substantial libration, possibly even some disorder, of the ring about the Mo—*Cp* vector.

The Cb ligand deviates only slightly from C_{4v} symmetry. Thus, the ring C—C bond lengths differ by only 0.013 (4) Å. Atoms C7, C9 and C11 are displaced by 0.340 (2), 0.562 (4) and 0.504 (3) Å, respectively, to the opposite side of the C_4 ring plane from the Mo atom, probably to relieve intraligand repulsions. Rotation of the $C7F_3$ group from its ideal position by *ca* 8° is shown by F1—C7—C6—C8 and F1—C7—C6—C10 torsion angles of 84.1 (3) and −67.6 (3)°, respectively. The near equality of the U_{eq} values for the Mo and the Cb ring C atoms is consistent with the high barrier to libration about the

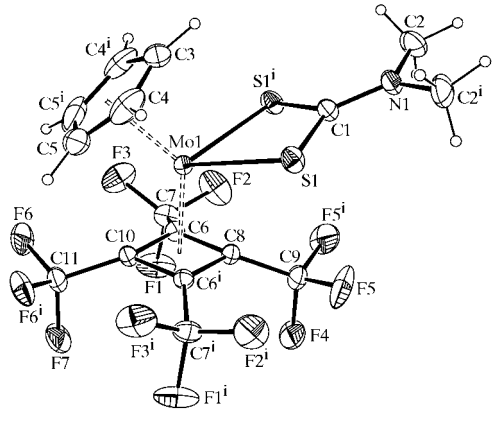


Figure 1
A view of the molecule of (I), showing 20% probability displacement ellipsoids. [Symmetry code: (i) x, $-y+\frac{1}{2}$, z.]

 DOI: 10.1107/S0108270105006086

Mo—*Cb* vector suggested by spectroscopic evidence (Davidson, 1987).

In other (η^4-C_4R_4)Mo complexes the ring C—C bond lengths usually show little variation and their average value of 1.462 (2) Å agrees well with the individual values in (I). In contrast, the ring C—C bond lengths in C_4R_4 molecules indicate fixed double and single bonds (Irmgartinger *et al.*, 1988, and references therein).

The Mo—C(Cb) bond lengths in (I) vary slightly and are on average 0.08 Å shorter than the mean value of 2.284 (7) Å for other (η^4-C_4R_4)Mo complexes (where R = Me, Ph, *etc.*). The displacement of the Mo atom from the Cb ring plane in (I) [1.944 (1) Å] is likewise less than the range of 1.995–2.074 Å found in other MoCb complexes.

Curnow *et al.* (1993) substantiate their view of Cb as a $C_4R_4^{2-}$ dianionic ligand from extended Hückel molecular-orbital (EHMO) calculations, which show that in CpCbMoL_2 species much more charge is transferred from Mo to Cb than to Cp. Electron-withdrawing CF_3 substituents on the Cb C atoms might be expected to facilitate this transfer and thus to produce the very strong Mo—Cb π bonds found in (I).

Experimental

The preparation and spectroscopic characterization of (I) have been described by Davidson (1987).

Crystal data

$[Mo(C_8F_{12})(C_5H_5)(C_3H_6NS_2)]$
M_r = 605.32
Monoclinic, $P2_1/m$
a = 8.918 (1) Å
b = 12.185 (1) Å
c = 9.809 (2) Å
β = 106.28 (1)°
V = 1023.2 (3) Å^3
Z = 2
D_x = 1.965 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.9–14.6°
μ = 0.96 mm^{-1}
T = 295 K
Prism, yellow
0.54 × 0.45 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled ω scans
Absorption correction: Gaussian (*ABSORB*; Mallinson & Muir, 1985)
T_{min} = 0.730, T_{max} = 0.800
5153 measured reflections
3025 independent reflections
2761 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 30.0°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = -13 \rightarrow 13$
2 standard reflections
frequency: 120 min
intensity decay: 0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.069
S = 1.06
3025 reflections
162 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.018P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0188 (13)

Table 1
Selected geometric parameters (Å, °).

Mo1—C3	2.309 (3)	Mo1—S1	2.4697 (5)
Mo1—C4	2.324 (2)	C6—C10	1.448 (2)
Mo1—C5	2.324 (2)	C6—C8	1.461 (2)
Mo1—C6	2.198 (2)	C6—C7	1.476 (3)
Mo1—C8	2.189 (2)	C8—C9	1.480 (3)
Mo1—C10	2.211 (2)	C10—C11	1.490 (4)
C10—C6—C8	88.85 (13)	C6—C10—C6^i	91.67 (19)
C6—C8—C6^i	90.61 (18)		
C10—C6—C8—C6^i	−1.0 (2)		

Symmetry code: (i) $x, -y+\frac{1}{2}, z$.

The structure was solved by Patterson and Fourier methods. H atoms were located initially in difference maps. In the final refinement, the positions of the H atoms were determined by the HFIX instruction in *SHELXL97* (Sheldrick, 1997) and they were then treated as riding on their parent C atoms [cyclopentadienyl C—H = 0.93 Å, methyl C—H = 0.96 Å and U_{iso}(H) = 1.3U_{eq}(C)]. A single parameter defining the orientation of the CH_3 group about the N—C bond was refined freely.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *GX* (Mallinson & Muir, 1985); program(s) used to solve structure: *GX*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank the EPSRC and Glasgow and Heriot–Watt Universities for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1377). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Curnow, O. J., Hirpo, W., Butler, W. M. & Curtis, M. D. (1993). *Organometallics*, **12**, 4479–4484.
Davidson, J. L. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2715–2722.
Drew, M. G. B., Felix, V., Goncalves, I. S., Romao, C. C. & Royo, B. (1998). *Organometallics*, **17**, 5782–5788.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Irmgartinger, H., Nixdorf, M., Riegler, N. H., Krebs, A., Kimling, H., Pocklington, J., Maier, G., Malsch, K.-D. & Schneider, K.-A. (1988). *Chem. Ber.* **121**, 673–677.
Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
Prout, K., Cameron, T. S., Forder, R. A., Critchley, S. R., Denton, B. & Rees, G. V. (1974). *Acta Cryst.* B**30**, 2290–2304.
Sheldrick, G. M. (1997) *SHELXL97*. University of Göttingen, Germany.