C5	0.3413 (2)	0.2587 (4)	0.3698 (3)	0.0283 (9)
C6	0.3718 (2)	0.3500 (4)	0.3129 (2)	0.0253 (8)
C7	0.6132 (2)	0.7735 (3)	0.2056 (2)	0.0214 (8)
C8	0.6327 (3)	0.8728 (4)	0.1356 (3)	0.0379 (10)
N1	0.4450 (2)	0.4077 (3)	0.3312 (2)	0.0182 (6)
N2	0.6250 (2)	0.4148 (3)	0.4960 (2)	0.0225 (7)
N3	0.5849 (2)	0.5240 (3)	0.3606 (2)	0.0180 (6)
O1	0.66296 (14)	0.5815 (2)	0.3755 (2)	0.0238 (6)
O2	0.56704 (15)	0.6838 (2)	0.1782 (2)	0.0211 (6)
O3	0.6439 (2)	0.7865 (2)	0.2869 (2)	0.0327 (7)
C98	0.4145 (3)	0.0859 (5)	0.1514 (4)	0.0597 (15)
C99	0.3214 (3)	0.0937 (4)	0.1358 (3)	0.0431 (11)
O99	0.2869 (2)	−0.0152 (3)	0.0956 (2)	0.0394 (7)

Table 2. *Selected geometric parameters (Å, °)*

Ni—N3	2.054 (3)	C4—C5	1.375 (5)
Ni—N1	2.116 (3)	C5—C6	1.383 (5)
Ni—O2	2.118 (2)	C6—N1	1.335 (4)
C1—N3	1.287 (4)	C7—O3	1.255 (4)
C1—N2	1.354 (4)	C7—O2	1.265 (4)
C1—C2	1.487 (5)	C7—C8	1.511 (5)
C2—N1	1.355 (4)	N3—O1	1.397 (3)
C2—C3	1.380 (5)	C98—C99	1.491 (7)
C3—C4	1.381 (5)	C99—O99	1.408 (5)
N3^{i}—Ni—N3	166.2 (2)	C2—C3—C4	118.9 (3)
N3^{i}—Ni—N1	93.92 (11)	C5—C4—C3	118.9 (3)
N3—Ni—N1	76.18 (11)	C4—C5—C6	119.2 (3)
N1—Ni—N1^{i}	89.7 (2)	N1—C6—C5	122.8 (3)
N3—Ni—O2^{i}	91.95 (10)	O3—C7—O2	124.7 (3)
N1—Ni—O2^{i}	89.64 (9)	O3—C7—C8	117.3 (3)
N3—Ni—O2	97.68 (10)	O2—C7—C8	117.9 (3)
N1—Ni—O2	173.76 (10)	C6—N1—C2	117.7 (3)
O2^{i}—Ni—O2	91.67 (13)	C6—N1—Ni	126.9 (2)
N3—C1—N2	124.6 (3)	C2—N1—Ni	115.4 (2)
N3—C1—C2	114.6 (3)	C1—N3—O1	112.1 (3)
N2—C1—C2	120.7 (3)	C1—N3—Ni	119.9 (2)
N1—C2—C3	122.5 (3)	O1—N3—Ni	127.8 (2)
N1—C2—C1	113.9 (3)	C7—O2—Ni	132.8 (2)
C3—C2—C1	123.6 (3)	O99—C99—C98	112.4 (4)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O99—H99···O3^{i}	0.84	2.08	2.909 (4)	172
O1—H1···O3	0.84	1.73	2.561 (3)	170
N2—H2*A*···O1	0.83	2.23	2.589 (4)	106
N2—H2*A*···O99^{ii}	0.83	2.36	3.086 (4)	146
N2—H2*B*···O2^{iii}	0.83	2.20	3.012 (4)	168

Symmetry codes: (i) $1 - x, y - 1, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, 1 - y, \frac{1}{2} + z$.

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, have been deposited with the IUCr (Reference: FG1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-(Benzenethiolato)bis(*tert*-butyl isocyanide)carbonyl(cyclopentadienyl)molybdenum(II), $[Mo(C_6H_5S)(C_5H_9N)_2(C_5H_5)(CO)]$

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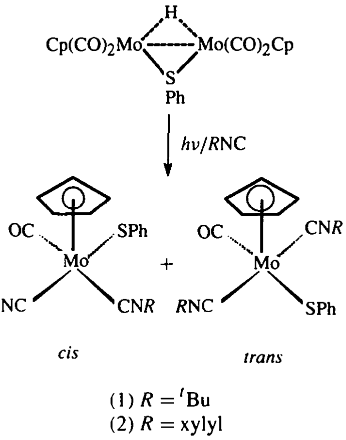
Abstract

In $[CpMo(SPh)(CO)(CN^tBu)_2]$, Cp = η^5-C_5H_5, the Mo atom adopts conventional four-legged piano-stool coordination geometry; a pair of *cis* CN^tBu ligands, together with carbonyl and benzenethiolato groups, make up the base. The Mo—CN^tBu bond lengths [2.053 (4) Å *trans* to S, 2.086 (4) Å *trans* to CO] show a small but significant difference.

Comment

While investigating the reactivity of the binuclear complex $[Cp_2Mo_2(\mu\text{-}H)(\mu\text{-}SPh)(CO)_4]$ (Schollhammer *et* *al.*, 1995), we obtained the mononuclear isocyanide complexes [CpMo(SPh)(CO)(CNR)$_2$]: (1) R = ^{t}Bu and (2) R = xylyl. At 293 K, solutions of both (1) and (2) contain two isomeric species. Thus, the ^{13}C NMR spectra show two signals of differing intensity for the CO and Cp ligands; the latter also displays two ^{1}H signals. For the CNR groups two patterns are also observed, one consisting of two signals of equal intensity, the other of a single signal. These results can be explained if solutions of (1) and (2) contain a mixture of *cis* and *trans* geometric isomers. The two isomers do not appear to interconvert readily between 293 and 353 K in solution. Although their relative abundances are different in different solvents, the *cis* form is always the major component. Only a single isomer of (1) could be obtained as a crystalline solid; when this solid was dissolved in toluene-d_8 at 210 K, the ^{1}H NMR spectrum at 210 K of the resulting solution indicated the presence of only the *cis* isomer.



To confirm this spectroscopic interpretation we have determined the structure of (1) by X-ray analysis (Fig. 1). As expected, the complex is a mononuclear 18-electron Mo$^{\text{II}}$ species. The metal atom adopts four-legged piano-stool coordination with *cis* isocyanide groups. Similar metal coordination occurs in the recently described complex [CpW(CO)$_2$(p-S-C$_6$H$_4$-CH$_3$)(CN^{t}Bu)] (Shaver, Hynes & Trojansek, 1994) which, like (1), exists as a mixture of isomers in solution; however, only the *trans* isomer of this tungsten compound could be obtained as a crystalline solid.

The Mo—S bond length in (1) [2.5040 (11) Å], though appreciably longer than the value of 2.408 Å suggested by Orpen *et al.* (1992) (hereafter OB92), appears quite typical of Mo—S distances in mononuclear CpMo(CO)(arylthiolate) species; a search of the Cambridge Structural Database (Allen *et al.*, 1979) gave a mean Mo—S bond length of 2.513 Å for 91 complexes of this type. Surprisingly, the μ_2-Mo—S distances of 2.416 (1)–2.420 (1) Å in [Cp$_2$Mo$_2$(μ-H)(μ-SMe)(CO)$_4$] (Schollhammer *et al.*, 1995) are 0.08 Å shorter than the terminal Mo—S distances in (1). The relative shortness of the Mo—CO bond length [1.923 (5) Å] in (1) compared with the mean value of 1.978 Å suggested by OB92 indicates stronger than usual back-donation from Mo to CO, the only strongly π-acidic ligand present. The Mo—CN^{t}Bu bond lengths differ by 0.033 (6) Å, the longer bond being *trans* to CO. This may reflect the greater *trans* influence of the π-acid CO compared with that of thiolate. The longest Mo—C(Cp) bond (to C31) is that most nearly *trans* to CO (see Fig. 1). There are previous suggestions that *trans* influence may be an explanation of bond-length trends in Mo piano-stool complexes (*e.g.* see Creswick & Bernal, 1982).

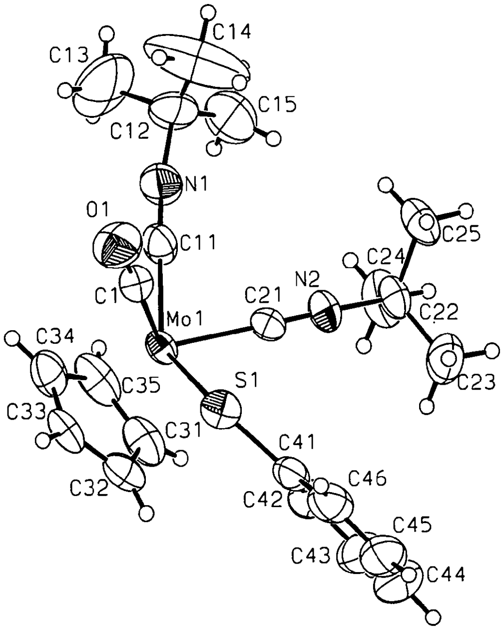


Fig. 1. Molecular structure of (1) with non-H atoms shown as 50% probability ellipsoids. H atoms are represented by spheres of arbitary radii.

Other structural features of (1) are unexceptional. The Mo atom lies almost in the benzenethiolate plane [Mo1—S1—C41—C42 = −9.1 (4)°]. The U_{eq} values for C atoms of the ^{t}Bu group attached to N1 are large and probably indicate disorder (see below).

Experimental

Reactions were performed under argon using standard Schlenk techniques and solvents were deoxygenated and dried by standard methods. [Cp$_2$Mo$_2$(μ-H)(μ-SPh)(CO)$_4$] (200 mg, 0.37 mmol) was dissolved in 30 ml of toluene together with 3 equivalents of isocyanide (1.1 mmol) and irradiated with UV light for 2 h. The solution changed from red to orange during this time. The solvent was removed under vacuum. The residue was then dissolved in the minimum amount of dichloromethane and chromatographed on a silica gel column. Elution with dichloromethane:tetrahydrofuran (100:1) gave an orange band of (1) which was washed with pentane. Recrystallization from diethyl ether gave (1) as an orange solid; yield 30%. Analysis: found C 55.7, H 6.0, N 5.8, S 6.5%; $C_{22}H_{28}MoN_2OS$ requires C 56.9, H 6.0, N 6.0, S 6.9%. NMR ($CDCl_3$, 293 K): ^{1}H δ 6.78–6.88, 6.96–7.07 (*m*), 7.40–7.47 (SC_6H_5); *cis* isomer 1.18 [9H, *s*, $C(CH_3)_3$], 1.48 [9H, *s*, $C(CH_3)_3$], 5.28 (5H, *s*, C_5H_5); *trans* isomer 1.26 [18H, *s*, $C(CH_3)_3$], 5.20 p.p.m. (5H, *s*, C_5H_5). $^{13}C\{^1H\}$ δ: *cis* isomer 30.38, 31.03 [$C(\underline{C}H_3)_3$], 56.95, 58.37 [$\underline{C}(CH_3)_3$], 91.82 (C_5H_5), 166.69, 170.95 (CN), 242.71 (CO); *trans* isomer 30.59 [$C(\underline{C}H_3)_3$], 57.86 [$\underline{C}(CH_3)_3$], 91.82 (C_5H_5), 178.32 (CN), 262.98 p.p.m. (CO). (2) was prepared in a similar way. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison. UV irradiations were performed using a Hanau TQ 150 mercury vapour lamp placed approximately 10 cm from a Pyrex vessel. Spectroscopic data for (1) and (2) have been deposited.

Crystal data

$[Mo(C_6H_5S)(C_5H_9N)_2(C_5H_5)(CO)]$
$M_r = 464.47$
Monoclinic
$P2_1/n$
$a = 10.6896 (9)$ Å
$b = 11.9963 (9)$ Å
$c = 18.399 (2)$ Å
$\beta = 98.748 (8)°$
$V = 2331.9 (4)$ Å^3
$Z = 4$
$D_x = 1.323$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 4.5–21.1°$
$\mu = 0.65$ mm^{-1}
$T = 294 (2)$ K
Needle
0.41 × 0.15 × 0.08 mm
Light orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.90$, $T_{max} = 0.96$
6360 measured reflections
6053 independent reflections

3775 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.026$
$\theta_{max} = 28.73°$
$h = 0 \rightarrow 14$
$k = -16 \rightarrow 0$
$l = -24 \rightarrow 24$
3 standard reflections frequency: 120 min intensity decay: 10.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.112$
$S = 1.064$
6052 reflections
250 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0320P)^2 + 0.7131P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Mo1	0.23047 (3)	0.15889 (3)	0.16553 (2)	0.03632 (10)
S1	0.07659 (10)	0.27857 (9)	0.21994 (6)	0.0486 (3)
O1	0.2439 (4)	0.3815 (3)	0.0819 (2)	0.0775 (11)
N1	0.5220 (4)	0.1762 (4)	0.1435 (2)	0.0706 (12)
N2	0.3959 (3)	0.1788 (3)	0.3272 (2)	0.0497 (9)
C1	0.2401 (4)	0.2984 (4)	0.1153 (2)	0.0480 (10)
C11	0.4167 (4)	0.1670 (4)	0.1504 (2)	0.0517 (11)
C12	0.6573 (4)	0.1911 (5)	0.1458 (3)	0.075 (2)
C13	0.6907 (7)	0.1382 (8)	0.0767 (4)	0.160 (4)
C14	0.6837 (7)	0.3113 (7)	0.1499 (7)	0.204 (6)
C15	0.7232 (5)	0.1322 (6)	0.2124 (3)	0.109 (2)
C21	0.3338 (3)	0.1772 (3)	0.2705 (2)	0.0406 (9)
C22	0.4761 (4)	0.1684 (4)	0.3987 (2)	0.0480 (10)
C23	0.3899 (5)	0.1771 (5)	0.4570 (2)	0.076 (2)
C24	0.5404 (5)	0.0563 (4)	0.4004 (3)	0.076 (2)
C25	0.5727 (5)	0.2613 (4)	0.4054 (2)	0.0653 (14)
C31	0.1723 (5)	−0.0317 (4)	0.1810 (3)	0.0625 (13)
C32	0.0628 (4)	0.0285 (4)	0.1573 (3)	0.0574 (12)
C33	0.0689 (4)	0.0730 (4)	0.0874 (2)	0.0533 (11)
C34	0.1841 (5)	0.0409 (4)	0.0669 (3)	0.0604 (12)
C35	0.2484 (5)	−0.0231 (4)	0.1252 (3)	0.0695 (15)
C41	0.0373 (4)	0.2323 (4)	0.3053 (2)	0.0503 (11)
C42	0.0710 (4)	0.1303 (4)	0.3380 (3)	0.0609 (13)
C43	0.0259 (5)	0.1005 (6)	0.4023 (3)	0.083 (2)
C44	−0.0487 (7)	0.1705 (7)	0.4353 (4)	0.102 (2)
C45	−0.0792 (5)	0.2718 (7)	0.4050 (4)	0.090 (2)
C46	−0.0367 (5)	0.3032 (5)	0.3406 (3)	0.0689 (14)

Table 2. *Selected geometric parameters (Å, °)*

Cp is the centroid of the cyclopentadienyl ring C31–C35.

Mo1—C1	1.923 (5)	Mo1—S1	2.5040 (11)
Mo1—C11	2.053 (4)	S1—C41	1.775 (5)
Mo1—C21	2.086 (4)	O1—C1	1.174 (5)
Mo1—C31	2.397 (4)	N1—C11	1.157 (5)
Mo1—C32	2.367 (4)	N1—C12	1.452 (6)
Mo1—C33	2.315 (4)	N2—C21	1.147 (5)
Mo1—C34	2.296 (4)	N2—C22	1.463 (5)
Mo1—C35	2.323 (5)		
Cp—Mo—S1	111.0	C41—S1—Mo1	115.7 (2)
Cp—Mo—C1	127.0	C11—N1—C12	172.1 (5)
Cp—Mo—C11	111.6	C21—N2—C22	174.2 (4)
Cp—Mo—C21	125.8	O1—C1—Mo1	177.2 (4)
C1—Mo1—C11	76.7 (2)	N1—C11—Mo1	176.8 (4)
C1—Mo1—C21	107.1 (2)	N2—C21—Mo1	174.0 (4)
C11—Mo1—C21	74.50 (15)	C46—C41—C42	117.8 (4)
C1—Mo1—S1	77.26 (13)	C46—C41—S1	116.8 (4)
C11—Mo1—S1	137.42 (13)	C42—C41—S1	125.4 (4)
C21—Mo1—S1	81.76 (11)		
Mo1—S1—C41—C42	−9.1 (4)	*Cp*—Mo1—S1—C41	74.2
C1—Mo1—S1—C41	−160.7 (3)	C11—Mo1—S1—C41	−107.2 (3)
C21—Mo1—S1—C41	−51.0 (2)		

The structure was solved by Patterson and Fourier methods. Anisotropic displacement parameters were refined for all non-H atoms. For H atoms the constraints C—H = 0.96 (methyl) or 0.93 Å (phenyl and Cp) and $U(H) = qU_{eq}(C)$ (q = 1.5 for methyl, 1.2 for Cp and phenyl) were applied. Orientation parameters for the six methyl groups were refined. Although the bond lengths and angles for the two CMe_3 groups compare well, apart from a slight shortening of C12—C14 [1.47 (1) Å] compared with the other C—CH_3 distances [1.50 (1)–1.52 (1) Å], the maximum U values for C13, C14 and C15 (0.31, 0.44, 0.16 Å^2) suggest positional disorder of these atoms; attempts to model this were not successful.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 Express*. Data reduction: *GX* (Mallinson & Muir, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We wish to thank EPSRC for equipment grant H24280.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and spectroscopic data for (1) and (2) have been deposited with the IUCr (Reference: CF1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^3-Allyl)dicarbonyl(1,10-phenanthroline)(trifluoroacetato)molybdenum, (I), and [*syn*(1,2,3-η)-2-Butenyl]dicarbonyl(1,10-phenanthroline)(trifluoroacetato)molybdenum, (II)

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Abstract

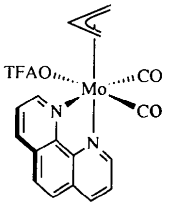
This structure determination shows that in the two molybdenum complexes of the title, (I), [Mo($C_2F_3O_2$)(C_3H_5)($C_{12}H_8N_2$)(CO)$_2$], and (II), [Mo($C_2F_3O_2$)(C_4H_7)($C_{12}H_8N_2$)(CO)$_2$], the phenanthroline ligand is perpendicular to the molybdenum–dicarbonyl plane. This is in contrast to similar molybdenum complexes, where the ligand is in the plane.

Comment

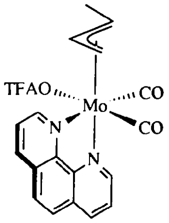
We have studied the nucleophilic substitution of allylic substrates for some time (Tsuji, 1980; Trost & Verhoeven, 1982; Heck, 1985; Collman, Hegedus, Norton & Finke, 1987; Godleski, 1991). A long-term goal is to find alternatives to the commonly used palladium catalyst by replacing palladium with other metals.

We have shown recently that (η^3-allyl)dicarbonyl(1,10-phenanthroline)molybdenum complexes are catalytically active in the nucleophilic substitution of allylic substrates, although there were major differences between the catalyses when the ligands were 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline (Sjögren, Frisell, Åkermark, Vitagliano & Eriksson, 1995). We postulate that the difference in the catalytic activities depends on the different geometries of the catalysts.

We have also shown that in solution, dicarbonyl(1,10-phenanthroline)[(1,2,3-η)-2-propenyl]molybdenum trifluoroacetate, which is one probable active catalyst, exists as an equilibrium of two complexes in a ratio of 1:2 (Sjögren, 1993). Similar behaviour has been reported earlier (Faller, Haitko, Adams & Chodosh, 1977, 1979) for a dicarbonyl(*P*–*P*)(η^3-allyl)molybdenum complex.



(I)



(II)

By the NOE technique it was shown that the major phenanthroline complex had the same geometry at Mo as that reported here for (I), and the geometry of the minor phenanthroline complex was shown to be the same as the earlier known dicarbonyl(*N*–*N*)(η^3-allyl)complexes. The work described here establishes that dicarbonyl(1,10-phenanthroline)[(1,2,3-η)-2-propenyl](trifluoroacetato)molybdenum, (I), and [*syn*-(1,2,3-η)-2-butenyl]dicarbonyl(1,10-phenanthroline)-(trifluoroacetato)molybdenum, (II), each have the molybdenum–phenanthroline plane perpendicular to the molybdenum–dicarbonyl plane. This is the same arrangement at Mo as reported for the dicarbonyl(*P*–*P*)(η^3-allyl)molybdenum complex but quite different from the earlier known dicarbonyl(*N*–*N*)(η^3-