Transition Metal–Cyanocarbon Chemistry.
Part V*. Crystal and Molecular Structures of Biscyclopentadienyl Complexes Containing a σ-Cyanoalkyl and a σ-Cyanoalkenyl Ligand: $(\eta^5\text{-}C_5H_5)_2Mo[S(C_6H_5)]\text{-}(\sigma\text{-}CH(CN){-}CH_3)$ and $(\eta^5\text{-}C_5H_5)_2Mo(S_2CN(C_2H_5)_2)(\sigma\text{-}C(CN){=}CH_2)$

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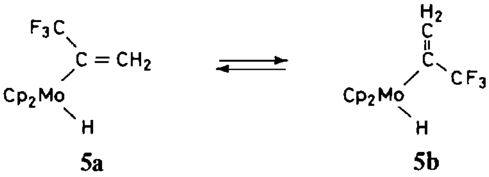
Abstract

The crystal structures of the title complexes were determined by X-ray diffraction analysis. $(\eta^5\text{-}C_5H_5)_2\text{-}Mo(SPh)(\sigma\text{-}CH(CN){-}CH_3)$–(4) crystallizes in the monoclinic space group $P2_1/c$ with a = 16.861(3), b = 7.570(4), c = 14.054(4) Å, β = 110.28(1)°, Z = 4. $(\eta^5\text{-}C_5H_5)_2Mo(S_2CN(C_2H_5)_2)(\sigma\text{-}C(CN){=}CH_2)$–(3) crystallizes in the monoclinic space group $P2_1/n$ with a = 21.943(3), b = 7.545(2), c = 11.325(1) Å, β = 98.33(1)°, Z = 4. The σ-alkyl ligand in (4) with Mo–C bond length of 2.306(3) Å has a perpendicular orientation with respect to the line bisecting the C_5H_5–Mo–C_5H_5 and S–Mo–C angles, but the conformation of the σ-alkenyl ligand in (3), with the corresponding Mo–C bond length of 2.232(4) Å, is parallel with respect to this line.

Introduction

Recently we reported the insertion reactions of mono- and dicyanoacetylenes into one or two metal–hydride bonds of biscyclopentadienyl dihydrides of molybdenum and tungsten Cp_2MH_2 (Cp = $\eta^5\text{-}C_5H_5$) [2]. Mono-inserted complexes $Cp_2MH(\sigma\text{-}C(CN){=}CHR)$–(1) R = H; (2) R = CN are attractive materials for further studies of the reactivity of the residual hydride as well as the unsaturated σ-alkenyl ligands. The complexes (1) and (2) were shown to undergo the substitution of thiolates, proceeding from ultraviolet irradiation of disulfides, for hydride ligand. This led to compounds of general formula $Cp_2MX(\sigma\text{-}C(CN){=}CHR)$–(3) [3]. The action of some protic reagents HX (X = Cl, O_2CCF_3, SPh) on (1) gave the protonation of σ-alkenyl ligand with the formation of σ-alkyl complexes of the type $Cp_2MX(\sigma\text{-}CH(CN){-}CH_3)$–(4). This study was enlarged on $Cp_2MoH(\sigma\text{-}C(CF_3){=}CH_2)$–(5) which upon the action of HO_2CCF_3 gave two isomers of a σ-alkyl complex (6): $Cp_2Mo(O_2CCF_3)(\sigma\text{-}CH(CF_3){-}CH_3)$–(6a) and $Cp_2Mo(O_2CCF_3)(\sigma\text{-}CH_2CH_2CF_3)$–(6b). We attributed the formation of these two isomers to the existence of different conformational orientation of the σ-alkenyl ligand in (5) [1, 4] and concluded that a 'parallel' conformation (a) gave (6a) and that a 'perpendicular' one (b) is a precursor for (6b) (Scheme 1). The formation of a single isomer in the case of compounds (4) which have the structure analogous to that of (6a) indicates that mono-inserted complexes (1) have a 'parallel' conformation. A variable temperature ^1H NMR study of (1) (M = Mo) revealed the existence of a sole isomer between −60 and +80 °C [3]. Because we are interested in the conformational structures of biscyclopentadienyl complexes and in the mechanisms of their reactions, the X-ray analyses were performed on one complex from the σ-alkyl family (4) Cp_2-



Scheme 1.

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*For Part IV, see ref. 1.

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TABLE I. Positional and Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2Mo(S(C_6H_5))(\sigma\text{-}CH(CN)\text{-}CH_3)$ (4).[a]

Atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Mo	0.29281(1)	0.19234(3)	0.29220(1)	0.00257(1)	0.00814(3)	0.00285(1)	−0.00048(3)	0.00202(1)	−0.0000(3)
S	0.27317(4)	0.0797(1)	0.44982(5)	0.00295(2)	0.0163(1)	0.00339(3)	−0.0018(1)	0.00221(4)	0.0021(1)
C(1)	0.3177(2)	0.0502(4)	0.1610(2)	0.0057(1)	0.0159(5)	0.0051(1)	−0.0042(5)	0.0069(2)	−0.0059(5)
C(2)	0.3328(2)	−0.0789(4)	0.2368(2)	0.0046(1)	0.0119(5)	0.0057(2)	0.0007(4)	0.0043(2)	−0.0050(5)
C(3)	0.2568(2)	−0.1075(4)	0.2545(2)	0.0059(1)	0.0083(5)	0.0059(2)	−0.0027(4)	0.0056(2)	−0.0039(5)
C(4)	0.1946(2)	0.0003(4)	0.1911(2)	0.0034(1)	0.0141(5)	0.0065(2)	−0.0031(4)	0.0020(2)	−0.0064(5)
C(5)	0.2317(2)	0.0964(4)	0.1311(2)	0.0057(1)	0.0142(5)	0.0032(1)	−0.0007(5)	0.0019(2)	−0.0018(5)
C(6)	0.3137(2)	0.4623(4)	0.2243(2)	0.0058(1)	0.0098(5)	0.0060(2)	−0.0027(4)	0.0062(2)	0.0016(5)
C(7)	0.2275(2)	0.4386(4)	0.2051(2)	0.0047(1)	0.0104(5)	0.0044(2)	−0.0006(4)	0.0002(2)	0.0025(5)
C(8)	0.2134(2)	0.4339(4)	0.2972(2)	0.0034(1)	0.0105(5)	0.0076(2)	0.0025(4)	0.0043(2)	0.0028(5)
C(9)	0.2934(2)	0.4568(4)	0.3740(2)	0.0061(1)	0.0088(4)	0.0042(1)	0.0005(4)	0.0034(2)	−0.0011(5)
C(10)	0.3539(2)	0.4770(4)	0.3278(3)	0.0034(1)	0.0086(4)	0.0075(2)	−0.0021(4)	0.0015(3)	−0.0009(5)
C(11)	0.1649(2)	−0.1803(4)	0.4589(3)	0.0041(1)	0.0174(6)	0.0073(2)	−0.0017(5)	0.0037(2)	0.0033(6)
C(12)	0.1712(2)	−0.0133(4)	0.4241(2)	0.00347(9)	0.0155(5)	0.0038(1)	−0.0026(4)	0.0033(2)	−0.0005(5)
C(13)	0.0975(2)	0.0769(5)	0.3751(3)	0.0036(1)	0.0241(7)	0.0107(3)	−0.0003(6)	0.0040(3)	0.0127(7)
C(14)	0.0194(2)	0.0001(7)	0.3598(4)	0.0032(1)	0.034(1)	0.0141(4)	−0.0014(7)	0.0025(4)	0.014(1)
C(15)	0.0143(2)	−0.1660(6)	0.3937(4)	0.0041(1)	0.034(1)	0.0112(3)	−0.0097(6)	0.0051(3)	0.0043(9)
C(16)	0.0873(3)	−0.2548(6)	0.4431(3)	0.0060(2)	0.0209(7)	0.0113(3)	−0.0088(6)	0.0060(3)	0.0054(8)
N	0.4670(2)	0.3049(4)	0.5700(2)	0.00349(9)	0.0235(6)	0.0050(1)	−0.0025(4)	0.0022(2)	−0.0053(5)
C(17)	0.4298(2)	0.1408(4)	0.3980(2)	0.00270(9)	0.0131(5)	0.0041(1)	0.0011(4)	0.0023(2)	0.0006(4)
C(18)	0.4493(2)	0.2319(4)	0.4938(2)	0.00238(9)	0.0140(5)	0.0054(2)	0.0007(4)	0.0023(2)	0.0019(5)
C(19)	0.4996(2)	0.1746(5)	0.3535(2)	0.0031(1)	0.0244(7)	0.0062(2)	0.0016(5)	0.0043(2)	0.0007(6)
H(1)	0.352(2)	0.084(4)	0.131(2)						
H(2)	0.385(2)	−0.123(4)	0.271(2)						
H(3)	0.254(2)	−0.184(4)	0.303(2)						
H(4)	0.145(2)	0.003(4)	0.184(2)						
H(5)	0.200(2)	0.163(4)	0.085(2)						
H(6)	0.337(2)	0.471(4)	0.187(2)						
H(7)	0.187(2)	0.427(4)	0.145(2)						
H(8)	0.168(2)	0.433(4)	0.301(2)						
H(9)	0.298(2)	0.452(4)	0.439(2)						
H(10)	0.408(2)	0.490(4)	0.358(2)						
H(11)	0.213(2)	−0.245(4)	0.489(2)						
H(13)	0.102(2)	0.190(4)	0.353(2)						
H(14)	−0.034(2)	0.051(4)	0.326(2)						
H(15)	−0.044(2)	−0.219(4)	0.378(2)						
H(16)	0.089(2)	−0.341(4)	0.465(2)						
H(17)	0.425(2)	0.017(4)	0.412(2)						
H(19A)	0.554(2)	0.145(4)	0.403(2)						
H(19B)	0.490(2)	0.107(4)	0.297(2)						
H(19C)	0.496(2)	0.305(4)	0.334(2)						

[a] Starred atoms were refined isotropically (B = 4 Å^2). The form of the anisotropic temperature factor expressions is: $\exp[-(B_{1,1} \times h2 + B_{2,2} \times k2 + B_{3,3} \times l2 + B_{1,2} \times hk + B_{1,3} \times hl + B_{2,3} \times kl)]$.

Mo(SPh)(σ-CH(CN)–CH$_3$) and on one complex from the σ-alkenyl family (3) Cp$_2$Mo(dtc)(σ-C(CN)=CH$_2$)–(dtc = S$_2$CN(C$_2$H$_5$)$_2$).

Experimental

Crystals of (4) [1] and (3) [3] suitable for X-ray diffraction studies were grown from CH$_2$Cl$_2$ solutions at room temperature. The space groups and approximate unit-cell dimensions were derived from Weissenberg photographs. Unit-cells were measured and intensity data collected on an Enraf-Nonius CAD4 diffractometer (Mo-K$_\alpha$, λ = 0.71073 Å).

Crystal Data for (4)

$C_{19}H_{19}MoNS$, M = 389.37, monoclinic, a = 16.861(3), b = 7.570(4), c = 14.054(4) Å, β = 110.28(1)°, U = 1578(4) Å^3, D_c = 1.64 g cm^{-3}, Z = 4, $F(000)$ = 792. Space group $P2_1/c$ (C_{2h}^5, No. 14), μ(MoK$_\alpha$) = 8.4 cm^{-1}. Crystal dimensions 0.08 × 0.45 × 0.22 mm. The intensities of 3688 reflexions

TABLE II. Positional and Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2Mo(S_2CN(C_2H_5)_2(\sigma\text{-}C(CN)=CH_2)$ (3).[a]

Atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Mo	0.33740(1)	0.27287(4)	0.53529(2)	0.00185(1)	0.01199(4)	0.00584(2)	0.00019(3)	0.00102(2)	0.00137(6)
S(1)	0.36291(4)	0.1088(1)	0.35973(8)	0.00209(2)	0.0187(2)	0.00853(7)	−0.00351(9)	0.00307(6)	−0.0064(2)
S(2)	0.47842(5)	0.3335(1)	0.3789(1)	0.00229(2)	0.0214(2)	0.01242(9)	−0.0046(1)	0.00301(7)	−0.0099(2)
C(1)	0.2557(2)	0.0938(5)	0.5045(3)	0.00213(7)	0.0181(7)	0.0073(3)	−0.0016(4)	0.0018(2)	0.0041(7)
C(2)	0.2443(2)	−0.0508(6)	0.4384(4)	0.00271(9)	0.0228(8)	0.0108(4)	−0.0041(5)	0.0029(3)	−0.0023(9)
C(3)	0.2076(2)	0.1382(6)	0.5733(3)	0.00263(9)	0.0231(8)	0.0095(3)	−0.0028(5)	0.0033(3)	0.0017(9)
N(1)	0.1712(2)	0.1790(6)	0.6312(4)	0.00340(9)	0.034(1)	0.0149(4)	−0.0025(5)	0.0077(3)	0.000(1)
C(4)	0.4314(2)	0.1788(5)	0.3090(3)	0.00188(7)	0.0148(6)	0.0077(3)	−0.0007(3)	0.0021(2)	−0.0000(7)
N(2)	0.4428(1)	0.1008(4)	0.2086(2)	0.00191(6)	0.0171(5)	0.0072(2)	−0.0013(3)	0.0019(2)	−0.0000(6)
C(5)	0.4016(2)	−0.0291(5)	0.1414(3)	0.00236(9)	0.0218(8)	0.0070(3)	−0.0010(5)	0.0012(3)	−0.0031(8)
C(6)	0.4129(2)	−0.2147(6)	0.1856(4)	0.0034(1)	0.0203(8)	0.0101(3)	−0.0038(5)	0.0021(3)	−0.0074(9)
C(7)	0.4979(2)	0.1459(5)	0.1547(3)	0.00221(8)	0.0176(7)	0.0099(3)	0.0008(4)	0.0037(2)	0.0017(8)
C(8)	0.4860(2)	0.2956(6)	0.0669(4)	0.0044(1)	0.0235(9)	0.0124(4)	0.0014(6)	0.0065(4)	0.010(1)
C(9)	0.2647(2)	0.4873(5)	0.5264(4)	0.00269(9)	0.0177(7)	0.0137(4)	0.0040(4)	0.0058(3)	0.0054(9)
C(10)	0.3199(2)	0.5652(5)	0.5726(4)	0.0047(1)	0.0111(6)	0.0098(3)	0.0027(5)	0.0019(4)	−0.0000(8)
C(11)	0.3597(2)	0.5656(5)	0.4833(4)	0.00237(9)	0.0157(7)	0.0119(4)	−0.0002(4)	0.0015(3)	0.0060(9)
C(12)	0.3272(2)	0.4905(5)	0.3834(3)	0.0031(1)	0.0179(7)	0.0079(3)	0.0023(4)	0.0025(3)	0.0088(7)
C(13)	0.2691(2)	0.4389(5)	0.4080(4)	0.00218(8)	0.0197(8)	0.0100(3)	0.0014(4)	−0.0000(3)	0.0065(8)
C(14)	0.4278(2)	0.2642(7)	0.6661(6)	0.0028(1)	0.040(1)	0.0223(6)	−0.0047(6)	−0.0058(4)	0.037(1)
C(15)	0.3850(3)	0.3001(8)	0.7244(5)	0.0065(2)	0.040(1)	0.0139(4)	0.0167(8)	−0.0099(4)	−0.024(1)
C(16)	0.3452(2)	0.174(1)	0.7241(4)	0.0029(1)	0.103(2)	0.0104(3)	0.005(1)	0.0030(3)	0.045(1)
C(17)	0.3666(3)	0.0440(6)	0.6602(5)	0.0083(2)	0.0183(7)	0.0302(6)	−0.0138(6)	−0.0229(5)	0.034(1)
C(18)	0.4184(3)	0.1046(8)	0.6265(4)	0.0061(1)	0.058(1)	0.0088(4)	0.0286(6)	−0.0013(4)	−0.001(1)
H(21)	0.205(1)	−0.108(5)	0.441(3)						
H(22)	0.273(2)	−0.094(5)	0.388(3)						
H(51)	0.364(2)	0.016(5)	0.144(3)						
H(52)	0.407(2)	−0.013(4)	0.059(3)						
H(61)	0.455(2)	−0.254(4)	0.179(3)						
H(62)	0.389(2)	−0.292(4)	0.133(1)						
H(63)	0.410(2)	−0.224(4)	0.269(3)						
H(71)	0.530(2)	0.178(5)	0.215(3)						
H(72)	0.508(2)	0.039(5)	0.112(3)						
H(81)	0.453(2)	0.270(4)	0.015(3)						
H(82)	0.523(2)	0.320(5)	0.031(3)						
H(83)	0.474(2)	0.392(5)	0.101(3)						
H(9)	0.230(2)	0.475(5)	0.560(3)						
H(10)	0.331(2)	0.604(5)	0.648(3)						
H(11)	0.397(2)	0.601(5)	0.492(3)						
H(12)	0.343(2)	0.469(5)	0.316(3)						
H(13)	0.243(2)	0.377(5)	0.360(3)						
H(14)	0.4608	0.3399	0.6535						
H(15)	0.3821	0.4093	0.7648						
H(16)	0.3088	0.1732	0.7607						
H(17)	0.3483	−0.0688	0.6425						
H(18)	0.4441	0.0408	0.5808						

[a] Starred atoms were refined isotropically (B = 4 Å^2) except the hydrogen atoms H(14) through H(18) which were placed from difference Fourier with the values of B fixed at 5 Å^2. The form of the anisotropic temperature factor expressions is: $\exp[-B_{1,1} \times h2 + B_{2,2} \times k2 + B_{3,3} \times l2 + B_{1,2} \times hk + B_{1,3} \times hl + B_{2,3} \times kl]$.

were measured using $\omega - 2\theta$ scan ($\theta_{min} = 2°$, $\theta_{max} = 28°$) from which 2506 independent planes with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

Crystal Data for (3)

$C_{18}H_{22}MoN_2S_2$, M = 426.46, monoclinic, a = 21.943(3), b = 7.545(2), c = 11.325(1) Å, β = 98.33(1)°, U = 1835(2) Å^3, D_c = 1.53 g cm^{-3}, Z = 4, F(000) = 872. Space group $P2_1/n$ (C_{2h}^5, No. 14) μ(MoK$_\alpha$) = 9.1 cm^{-1}. Crystal dimensions 0.10 × 0.70 × 0.10 mm. 2816 independent reflexions ($\theta < 28°$) with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

All calculations were carried out using the Enraf-Nonius SDP program library [5]. Both structures were solved and refined by conventional three-dimensional Patterson, difference Fourier and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters and the difference Fourier maps at this stage gave the positions of hydrogen atoms. Final refinements (x, y, z-all atoms including hydrogens), B_{ij} for Mo, S, C and N atoms, secondary extinction and isotropic thermal parameters for all refined hydrogens fixed at 4.0 Å^2 and at 5.0 Å^2 for five hydrogens in (**3**) placed by calculations, led to the following residuals: (**4**): $R = 0.026$, $R_w = 0.034$ and (**3**): $R = 0.030$, $R_w = 0.041$. The weighting scheme employed was $w^{-1} = \sigma^2(F) = \frac{1}{4}[\sigma(I)/(I) + 0.06^2(I)]$. The final atomic coordinates and thermal parameters are given in Table I [for (**4**)] and II [for (**3**)] and the bond distances and angles in Tables III [for (**4**)] and IV [for (**3**)]. Tables of observed and calculated structures factors may be obtained from the authors.

TABLE III. Interatomic Distances (Å) and Bond Angles (deg), with e.s.d.s in Parentheses for (4).

Distances		Angles	
Mo–S	2.500(1)	C(17)–Mo–S	77.39(8)
Mo–C(17)	2.306(3)	C(17)–Mo–CY1	104.4
Mo–CY1[a]	1.986	C(17)–Mo–CY2	105.3
Mo–CY2[a]	1.988	S–Mo–CY1	106.5
C(17)–H(17)	0.964(37)	S–Mo–CY2	109.6
C(17)–C(18)	1.445(4)	CY1–Mo–CY2	137.1
C(17)–C(19)	1.534(4)	Mo–C(17)–C(18)	112.0(2)
C(18)–N	1.149(4)	Mo–C(17)–C(19)	116.6(2)
S–C(12)	1.775(3)	Mo–S–C(12)	111.8(1)
		C(18)–C(17)–C(19)	109.9(3)
		C(17)–C(18)–N	178.2(3)

[a] CY is the gravity center of C_5H_5 ring.

TABLE IV. Interatomic Distances (Å) and Bond Angles (deg), with e.s.d.s in Parentheses for (3).

Distances		Angles	
Mo–S(1)	2.474(1)	S(1)–Mo–C(1)	80.9(1)
Mo–C(1)	2.232(4)	Mo–S(1)–C(4)	114.4(1)
Mo–CY1[a]	1.985	Mo–C(1)–C(2)	131.9(3)
Mo–CY2[a]	1.986	Mo–C(1)–C(3)	114.2(3)
C(1)–C(2)	1.326(6)	C(2)–C(1)–C(3)	113.9(4)
C(1)–C(3)	1.439(6)	C(1)–C(3)–N(1)	176.8(5)
C(3)–N(1)	1.147(5)	S(1)–C(4)–S(2)	123.3(2)
S(1)–C(4)	1.766(4)	S(1)–C(4)–N(2)	114.7(3)
S(2)–C(4)	1.678(4)	S(2)–C(4)–N(2)	122.0(3)
C(4)–N(2)	1.336(4)	C(4)–N(2)–C(5)	123.9(3)
N(2)–C(5)	1.469(5)	C(4)–N(2)–C(7)	121.3(3)
N(2)–C(7)	1.471(4)	C(5)–N(2)–C(7)	114.8(3)
C(5)–C(6)	1.496(6)	N(2)–C(5)–C(6)	113.0(3)
C(7)–C(8)	1.503(7)	N(2)–C(7)–C(8)	112.0(4)
		CY1–Mo–CY2	136.7

[a] CY is the gravity center of C_5H_5 ring.

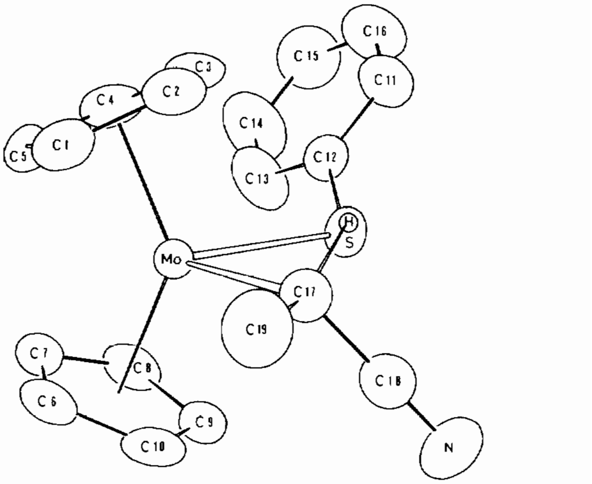


Fig. 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Mo(S(C_6H_5(\sigma\text{-}CH(CN)\text{-}CH_3)$ (4).

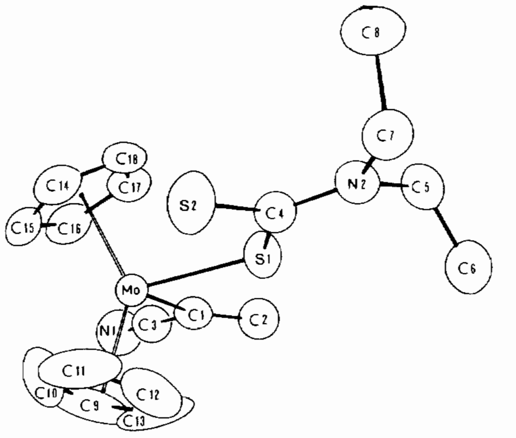


Fig. 2. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Mo(S_2CN(C_2H_5)_2)(\sigma\text{-}C(CN){=}CH_2)$ (3).

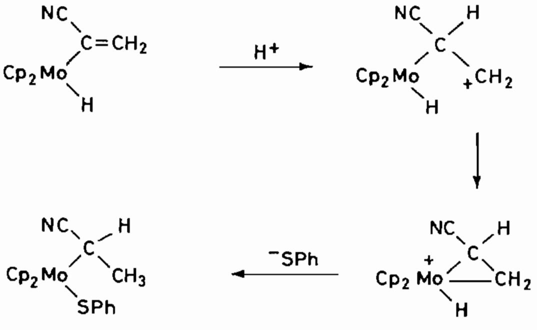
Results and Discussion

The crystal structures of (**4**) and (**3**) consist of discrete $Cp_2Mo(SPh)(\sigma\text{-}CH(CN)\text{-}CH_3)$ (Fig. 1) and $Cp_2Mo(dtc)(\sigma\text{-}C(CN){=}CH_2)$ (Fig. 2) molecules, respectively, in which the molybdenum atoms have a formal tetrahedral coordination and use eight of their nine valence orbitals in the bonding with ligands. This geometry is typical of bent biscyclopentadienyl complexes [6]. The most interesting features of the structure determinations of both complexes are the conformational orientations of the σ-alkyl and σ-alkenyl ligands, as well as the lengths of the molybdenum–carbon σ-bonds. The Mo–C bond lengths in (**4**) (2.306(3) Å) and (**3**) 2.232(4) Å) are significantly shorter than the molybdenum–alkyl σ-bond length of *ca.* 2.38 Å [7], but are much greater than the distance of 1.833(6) Å found in a carbene complex $Cp[P(OMe)_3]_2ClMo{=}C{=}C(CN)_2$

[8] and of 2.13(1) Å observed in the metallacyclopropene complex $Cp_2Mo(C_2(CF_3)_2)$ [9]. The molybdenum–carbon (σ-alkyl) bond length in (**4**) is very close to that observed by Prout in $Cp_2MoCl(\sigma\text{-}CH_2CH_3)$ (2.284(10) Å) [6], and the corresponding molybdenum–carbon (σ-alkenyl) bond length in (**3**) is very close to that found in $Cp_2MoH[(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)]-$ (2.223(6) Å [10]:

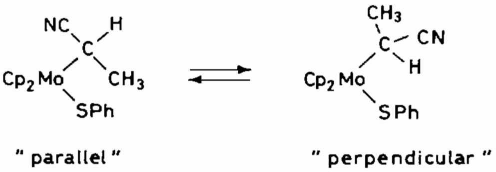
The difference between molybdenum–carbon distances in the σ-alkyl and σ-alkenyl bonds of 0.07 Å, although higher than the value of 0.03 Å proposed by Churchill for the difference in covalent radii of sp^3 and sp^2 hybridized carbon atoms [7] seems to be attributable to this latter phenomenon. Moreover, the double bond activated by the electron withdrawing groups (CN, CO_2Me) can give rise to the increase of the strength of the metal–ligand σ-bonds as a result of contraction of the molybdenum d-orbitals. As a consequence the Mo–S(dtc) distance (2.474(1) Å) is shorter in the σ-alkenyl complex (**3**) than is the Mo–S(SPh) distance (2.500(1) Å) in the σ-alkyl one (**4**). Both molybdenum–sulfur bond lengths lie in the range observed for Mo(IV) complexes (2.43–2.51 Å) [11, 12]. The dithiocarbamate ligand in (**3**) is strictly monodentate (Mo–S(2) separation of 3.8 Å is too long to indicate any interaction) and lies roughly in the plane bisecting the Cp–Mo–Cp angle. The dihedral angle between the plane of S(1), S(2), C(4), N(2), C(5) and C(7) atoms and S(1)–Mo–C(1) plane is equal to 4.9°. The observed monodentate nature of the dtc ligand is confirmed by the carbon–sulfur distances. The single C(4)–S(1) bond length of 1.766(4) Å is only slightly shorter than the corresponding bond lengths in dithiocarbamate-like mono- and disulfides (tmtm: tetramethylthiuram monosulfide [13], dptm: dicyclopentamethylenethiuram monosulfide [14] and tetd: tetraethylthiuram disulfide [15], ranging from 1.783(4) to 1.81(1) Å. The formally double C(4)–S(2) bond of 1.678(4) Å is close to the analogous bonds in tmtm, dptm and tetd (1.636(6)–1.66(1) Å), but shorter than the corresponding distances observed in the mercury–dtc complexes (1.70–1.74 Å) [16–18] where the dtc ligand has some chelating nature.

The carbon–carbon bond in the σ-alkyl ligand of (**4**) is nearly perpendicular to the line bisecting the Cp–Mo–Cp and S–Mo–C planes ('perpendicular' conformer analogous to (**5b**) represented in Scheme 1), but the carbon–carbon bond in the σ-alkenyl ligand of (**3**) is nearly parallel to this line ('parallel' conformer analogous to (**5a**) in Scheme 1). Complex (**4**) results from protonation of the unsaturated carbon–carbon bond in (**1a**). The mechanism of this reaction (Scheme 2) involves a 'parallel' conformer of the parent complex (see Introduction) [1]).



Scheme 2.

The formation of the 'perpendicular' conformation of the σ-alkyl ligand implies a rotation of the initial 'parallel' configuration of the σ-alkenyl ligand in (**1a**) around the molybdenum–carbon bond. Such a rotation (Scheme 3) should operate at the final step



Scheme 3.

of the mechanism depicted in Scheme 2 and must be due to steric hindrances. The methyl group of the ligand is better accomodated with respect to the two Cp rings in the 'perpendicular' conformer than the nitrile and hydrogen substituents on the assymetric carbon atom do. A 'parallel' conformation in (**4**) should lead to a too high differentiation of the Cp rings.

The 'parallel' conformation of σ-alkenyl ligand in (**3**) indicates that there is no rearrangement of the ligand orientation upon the action of tetd and probably of other disulfides on (**1**) [3].

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