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THE ABSOLUTE CONFIGURATION OF ORGANOMETALLIC COMPOUNDS

VII *. AN X-RAY STRUCTURAL STUDY OF $(-)_{579}$-$(+)_{436}$-$(\eta^5$-$C_5H_5)Mo(CO)_2[(C_5H_5N)C(=S)NR^*]$ PREPARED FROM H_2NR^* = (*S*)-(—)-α-PHENYLETHYLAMINE

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Summary

The reaction of $(\eta^5$-$C_5H_5)Mo(CO)_3Cl$ with pyridine-2-carboxylic acid [(*S*)-1-phenylethylthioamide] yields two diastereoisomers having composition $(\eta^5$-$C_5H_5)Mo(CO)_2$(thioamide) which are in equilibrium with one another in the ratio of 58/42 (toluene; 90°C). The diastereoisomers are separable by chromatography, and that (V; see text) whose CD spectrum shows (—) and (+)-bands, respectively, at 579 and 436 nm was used in the current crystallographic study. The space group is $P2_12_12_1$ and the cell parameters are: *a* 6.950(4), *b* 14.038(4) and *c* 20.709(8) Å; *V* 2020.4 Å^3; *d*(obs; flotation in aqueous $ZnBr_2$) 1.51 g cm^{-3}; *d*(calc; *Z* = 4) 1.507 g cm^{-3}. A total of 3321 data were recorded in one octant of reciprocal space ($2\theta_{max}$ 60.0°) of which 2134 were considered observed ($I > 2\sigma(I)$) and used in the solution of the structure and in the least-squares refinement. The molecules consist of a central Mo atom surrounded by an approximately square-pyramidal array of five ligands: the bidentate thioamide, two carbonyls and the Cp ring. The binding points of the thioamide are the nitrogen of the pyridine and the sulfur of the thioamide moiety. Thus, unlike previous examples of $CpMo(CO)_2$(thioamides) studied here, the nitrogen of the thioamide is not part of the chelate ring; instead, it is part of an unusual, three atom, conjugated system (S—C—N) never observed before in thioamide-metal chelates. The S—Mo—N, S—Mo—C(O), N—Mo—C(O) and (O)C—Mo—C(O) angles are 76.9(2), 75.2(3), 81.4(4) and 75.6(5)°, values which are typical of square-pyramidal compounds in which the metal is above the plane defined by the basal ligands. The bonds to the carbons of the C_5H_5 ring are normal but the two Mo—C(O) and the two C—O distances are slightly different, and the differences make sense if we attribute them to inequalities in *trans* effect

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* For part VI see ref. 6.

between S and N ligands opposite the carbonyls. The Mo—N(pyridine) bond (2.233(8) Å) is a little longer than those observed in thioamides but nearly the same as that observed in Schiff base derivatives of related $CpMo(CO)_2$ compounds studied here earlier. Concomitantly, in V there is a shorter Mo—S bond than those observed in the thioamides containing normal, four-membered (Mo—S—C—N) chelate rings. Parallel with this, V contains longer S—C bonds showing that an increase in the Mo—S bond order leads to a reduction of the S—C π-bond order, which in this case is estimated to be only 0.47. Finally, the plane of the chelate ring (Mo—S—C—C—N) and that of the pyridine ring make an angle of 8.7°, even though the two are fused to each other. The absolute configuration at the Mo site of the $[(-)_{579}, (+)_{436}]$ diastereoisomer has been established as (*S*).

Introduction

Some time ago, we reported the crystal structures and absolute configurations of a number of square-pyramidal [3—5] and tetrahedral [6—8] organometallic complexes in which the metal is an asymmetric center. In order to assign identification lables to the absolute configurations of the molecules we are dealing with, it is first necessary to set down some definitions.

(a) Sequence of ligands defining a rotational or chiral sense. We use the suggestions of Stanley and Baird [1] who extended the *R,S* system of Cahn, Ingold and Prelog [2] to *polyhapto* ligands of organometallic compounds. Accordingly, a rotational sense (1 → 2 → 3) is established. We call the plane defined by the three highest ranking ligands the chirality defining plane.

(b) Line of sight of the observer. In order to attach a symbol (*R* or *S*) to the rotational sense mentioned in (a), the location of the observer has to be specified. In accordance with the convention of Cahn, Ingold and Prelog [2], the observer

TABLE 1

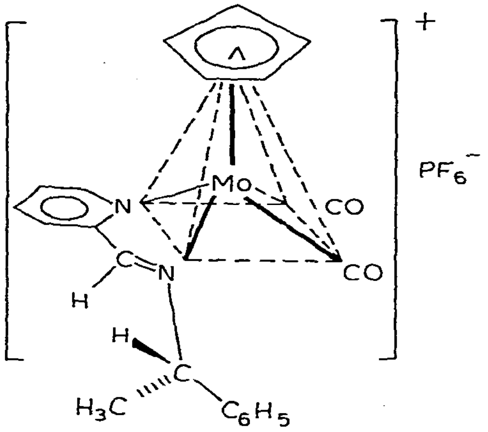
SQUARE PYRAMIDAL COMPOUNDS (I—III) AND TETRAHEDRAL COMPOUNDS

Compound	Preferred [a] diastereoisomer	CD rotation at 579 nm	Chirality symbol [c] at metal atom	Reference
I [b]	No	(+)	*R*	3
II	Yes	(—)	*S*	4
IV	Yes	(—)	*S*	5
Tetrahedral compounds				
VI	Yes	(—)	*R*	6
VII	Yes	(—)	*S*	7

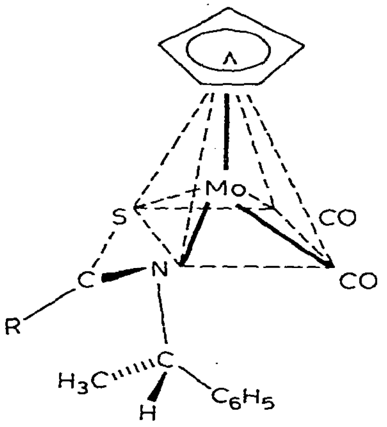
[a] A diastereoisomer is said to be preferred if it exists in solution, at equilibrium, as the predominant species. Nature of solvents and temperatures at which these measurements were done are reported in the references given. In all cases, the absolute configurations determined here are those of the diastereoisomer listed in the second column of this table. [b] In line with the conventions set at the beginning of the Introduction, the correct chirality symbol for the configuration at the metal atom of this diastereoisomer is opposite to that given in the original report [3]. This reversal is necessitated by the definition for the "Line of sight of the observer" given in (b). [c] Although the configuration around the chiral carbon was unknown to us at the beginning, it was found to be (*S*) for compounds I and II and (*R*) for IV, always in agreement with the optically active amine used in the syntheses.

is located on the side of the plane (defined above, (a)) opposite to the lowest ranking group(s).

Therefore, we select the chirality defining plane as described in (a) and attach

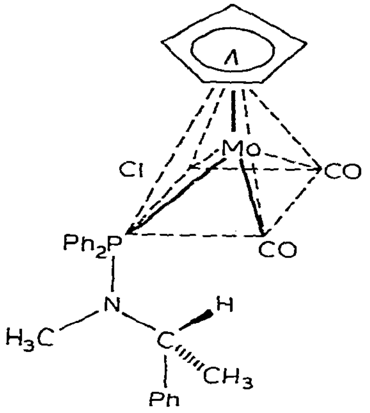


(I)

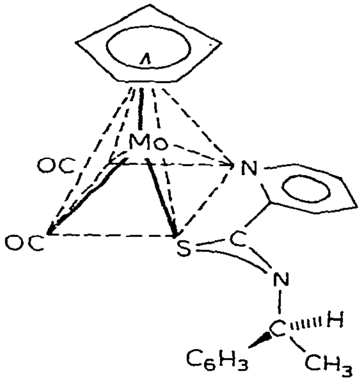


(II) R = CH_3

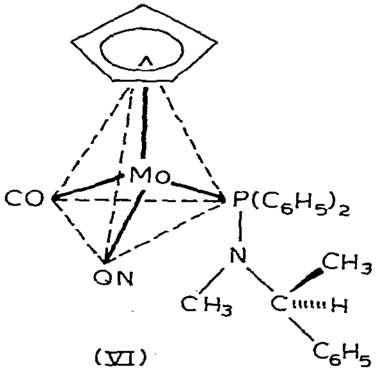
(III) R = pyridine



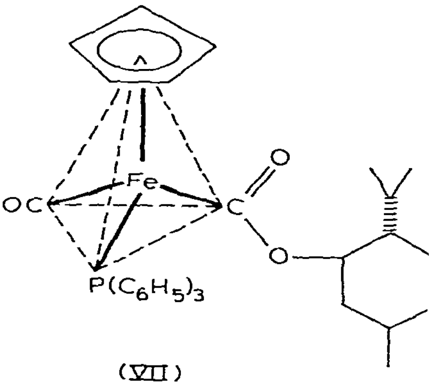
(IV)



(V)



(VI)



(VII)

a symbol (*R* or *S*) according to whether the rotational sense implied by the sequence of ranking ligands 1, 2 and 3 is clockwise or anti-clockwise when viewed as specified in (b). Such a convention defines the diastereoisomer uniquely if the configuration around the Mo atom is tetrahedral or in square pyramidal compounds when the two ligands of rank lower than the third are chemically equivalent, as in compounds I, II, IV and V. However, if these ligands are not identical two stereoisomers (and four diastereoisomers) are possible. In that case the *RS* notation is completely incapable of differentiating between them.

On the basis of the above rules, the symbols of the diastereoisomers thus far determined in this group, and mentioned in this study, are listed for the convenience of the reader in Table 1.

Sometime ago, we reported the structure and absolute configuration of cation I [3] and of the neutral thioamide II [4], both of which contain a Mo atom as the chiral center. Furthermore, in both compounds the central metal atom is part of a $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ moiety bound to a bidentate ligand which completes the coordination sphere. The differences between the two systems are: (a) in I, the MoL_2 fragment (L_2, the bidentate ligand = a Schiff base) consists of a five-membered ring in which the two binding atoms are nitrogens. In II, the ring is four-membered and L_2 = a thioamide of which the binding points are one N and one S. (b) the structure and absolute configuration determined for I was that of the non-preferred diastereoisomer (see ref. 8 for details) while in the case of II we determined the absolute configuration of the preferred diastereoisomer (see ref. 9 for details). Table 1 states that I is the non-preferred diastereoisomer, that it rotates (+) at 579 nm and that its absolute configuration is *R*, while II is the preferred diastereoisomer, it rotates (—) at 579 nm and the absolute configuration at the metal atom is *S*; i.e., there is an exact enantiomorphism of physical properties for this pair. Inasmuch as I and II are very different, it is fair to ask whether this apparent correlation is a mere accident or not. Also we note that IV, which is vastly different from either I or II seems to fall in line with the correlation of physical properties vs. absolute configuration. Therefore, when Brunner and Spettel [10] carried out the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2Cl$ with pyridine-2-carboxylic acid [(*S*)-1-phenylethylthioamide] it became important for us to determine whether the product was III, V or the isomer of V in which the N of the thioamide (and not the S) was the second binding point. Brunner and Spettel [10] have carried out detailed studies which led them to postulate V as the correct structure. Thus, determining which of the three structural possibilities is correct and the relationship between the CD rotation, absolute configuration and the preferredness of the diastereoisomer would be important for our attempts to establish useful correlations in this new field of optical active organometallics.

Experimental

The syntheses, isolation and physical properties of $(-)_{579}\text{-}(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{-}[(C_5H_4N)C(S)NCH(CH_3)(C_6H_5)]$ have been given elsewhere [10]. A crystal of irregular shape was mounted on a goniometer head and placed on an ENRAF-NONIUS CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and data processing is

TABLE 2

CRYSTALLOGRAPHICALLY IMPORTANT DATA COLLECTION AND DATA PROCESSING INFORMATION

Empirical formula	$MoSN_2O_2C_{21}H_{18}$
Molecular weight	458.39 g mol^{-1}
Cell constants	a 6.950(4) Å
	b 14.038(4) Å
	c 20.709(8) Å
Unit cell volume	V 2020.4 Å^3
Space group	$P2_12_12_1$
Number of molecules in unit cell	$Z = 4$
Density	ρ(calc.) 1.507 g cm^{-3}
	ρ(obs.) 1.51 g cm^{-3}
Absorption coefficient (Mo-K_α)	μ 7.56 cm^{-3}
Radiation used for data collection	Mo-K_α (λ 0.71069 Å)
Scanning range for 2θ	$6.00° < 2\theta < 60.00°$
Standards for intensity control (every 40 reflections)	[2,3,7 and 3,4,6]
Scan width for each reflection	$\Delta\theta = (0.80 + 0.40 \tan \theta)°$
Maximum scan time	3 minutes
Minimum number of counts above background for each reflection	2000
Scan technique	$\theta - 2\theta$
Range of scan speeds	0.4 to 5.0°/min
Total number of reflections collected [a]	3321
Number of contributing reflections in the last least-squares [b]	2134
Number of variables	316
Weighting scheme	$w = 1/\sigma^2(F_0)$
Final $R(F)$ [c]	0.046
Final $R_w(F)$ [d]	0.049

[a] A total of 3321 reflections were collected of which 2134 having $I > 2\sigma(I)$ were classified as "observed" with the remaining 1287 being termed "less-thans". [b] 2134 "observed" and 1287 "less-thans", for which $I > 2\sigma I$. [c] $R(F) = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [d] $R_w(F) = [\Sigma_w||F_0| - |F_c||^2/\Sigma_w|F_0|^2]^{1/2}$.

given in Table 2. Accurate cell constants determination and data collection were similar to those described in detail elsewhere [11] and are thus not repeated here.

Solution and refinement

Data decoding was accomplished using a locally written program (Houston). Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_0|$. No absorption corrections were made due to the low value of the absorption coefficients (μ 7.6 cm^{-1}). Standard deviations of the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{Tot} + 2\ \Sigma I_{BG}$. Standard deviations in the structure factor amplitues, $\sigma(|F_0|)$, were estimated as $\sigma(|F_0|) = \sigma(I)/2Lp|F_0|$. All data processing and calculation were carried out using the X-ray '72 System of programs [12].

A three dimensional Patterson map was computed and the positions of the Mo atoms were determined. All the remaining nonhydrogen atoms were easily found from successive difference Fourier maps. Full-matrix least-squares refinement with isotropic models for all the nonhydrogen atoms gave $R(F) = 0.101$. Hydrogen atoms were added at theoretically calculated positions (C—H 0.95 Å). Further anisotropic refinement of the nonhydrogen atoms and isotropic refine-

TABLE 3

FINAL POSITIONAL PARAMETERS OF THE NON HYDROGEN ATOMS

Atom	X	Y	Z
Mo	0.09068(13) [a]	0.24785(9)	0.21045(4)
S	−0.0063(6)	0.0970(2)	0.1576(2)
N(1)	−0.1081(13)	0.2966(5)	0.1324(3)
N(2)	−0.2775(14)	0.0800(6)	0.0634(4)
C(1)	0.3162(18)	0.3724(9)	0.2073(8)
C(2)	0.3379(21)	0.3259(12)	0.1475(7)
C(3)	0.3919(20)	0.2317(9)	0.1566(7)
C(4)	0.4153(21)	0.2188(10)	0.2275(8)
C(5)	0.3621(22)	0.3064(13)	0.2566(6)
C(6)	−0.0867(20)	0.3199(11)	0.2629(6)
C(7)	0.0307(20)	0.1587(8)	0.2837(6)
C(8)	−0.1261(17)	0.3923(7)	0.1229(5)
C(9)	−0.2247(19)	0.4285(7)	0.0711(5)
C(10)	−0.2906(18)	0.3709(8)	0.0233(5)
C(11)	−0.2733(17)	0.2721(8)	0.0319(5)
C(12)	−0.1790(13)	0.2407(9)	0.0879(4)
C(13)	−0.1688(15)	0.1301(8)	0.0972(4)
C(14)	−0.2763(21)	−0.0254(8)	0.0770(6)
C(15)	−0.4884(21)	−0.0558(10)	0.0769(7)
C(16)	−0.1583(17)	−0.0727(7)	0.0256(6)
C(17)	−0.2056(20)	−0.0672(8)	−0.0406(6)
C(18)	−0.0935(25)	−0.1150(9)	−0.0862(6)
C(19)	0.0626(22)	−0.1703(9)	−0.0687(7)
C(20)	0.1085(20)	−0.1777(8)	−0.0041(8)
C(21)	−0.0030(20)	−0.1312(8)	0.0417(6)
O(1)	−0.1921(14)	0.3628(8)	0.2955(4)
O(2)	−0.0017(17)	0.1135(7)	0.3265(4)

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[a] Numbers in parentheses are the estimated standard deviations in the least significant digits in this and in succeeding tables.

TABLE 4

THEORETICAL POSITIONS OF THE HYDROGEN ATOMS [a] (Calculated after $R(F) = 4.6\%$)

Atom	X	Y	Z
H(1)	0.2776	0.4367	0.2135
H(2)	0.3182	0.3550	0.1066
H(3)	0.4104	0.1848	0.1241
H(4)	0.4575	0.1629	0.2491
H(5)	0.3579	0.3187	0.3017
H(8)	−0.0688	0.4349	0.1529
H(9)	−0.2474	0.4957	0.0687
H(10)	−0.3467	0.3967	−0.0147
H(11)	−0.3232	0.2285	0.0011
H(14)	−0.2194	−0.0378	0.1179
H(17)	−0.3138	−0.0309	−0.0541
H(18)	−0.1256	−0.1094	−0.1307
H(19)	0.1367	−0.2025	−0.1005
H(20)	0.2163	−0.2145	0.0090
H(21)	0.0276	−0.1396	0.0860
H(151)	−0.5422	−0.0404	0.0361
H(152)	−0.4942	−0.1228	0.0833
H(153)	−0.5632	−0.0259	0.1095

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[a] The numbering system of the hydrogens is such that its number is identical to that of the carbon it is attached to.

TABLE 5

THERMAL PARAMETERS (X 10^3) [a] OF THE NONHYDROGEN ATOMS

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	42.0(8)	56.3(9)	42.1(8)	—7.1(1.0)	—3.5(6)	—1.5(8)
S	74(3)	43(2)	79(2)	2(2)	—30(2)	6(2)
N(1)	34(5)	46(5)	43(5)	—26(5)	0(5)	—9(4)
N(2)	54(7)	51(6)	47(5)	0(6)	—6(5)	—2(5)
C(1)	46(8)	78(9)	94(10)	—13(8)	10(10)	—18(10)
C(2)	62(12)	113(14)	84(11)	1(11)	21(9)	16(11)
C(3)	42(8)	70(11)	100(10)	—5(10)	19(9)	—2(8)
C(4)	30(7)	110(14)	103(13)	—5(9)	2(10)	0(9)
C(5)	50(12)	117(12)	64(10)	—13(10)	—6(8)	—17(10)
C(6)	49(9)	153(14)	50(8)	—61(11)	7(8)	—46(9)
C(7)	87(12)	51(8)	85(10)	—34(8)	—3(14)	27(8)
C(8)	59(9)	49(7)	56(7)	—4(8)	—3(7)	3(6)
C(9)	64(9)	46(7)	72(8)	—5(7)	—14(8)	21(6)
C(10)	66(9)	65(8)	46(7)	10(8)	—3(7)	21(6)
C(11)	50(8)	51(9)	49(6)	—2(7)	2(6)	—10(6)
C(12)	33(6)	59(8)	40(5)	—15(9)	11(5)	—20(7)
C(13)	28(6)	64(8)	42(6)	—16(7)	—7(5)	7(6)
C(14)	75(11)	41(8)	69(9)	0(9)	4(9)	4(7)
C(15)	71(10)	83(10)	87(10)	—21(9)	12(9)	—7(9)
C(16)	47(8)	17(6)	67(8)	—9(6)	—19(7)	—1(6)
C(17)	68(10)	42(8)	69(9)	—9(8)	2(8)	—2(7)
C(18)	104(13)	54(9)	73(9)	—15(11)	10(12)	—1(8)
C(19)	64(11)	44(8)	105(11)	—16(9)	13(10)	—22(8)
C(20)	56(10)	31(7)	138(12)	5(8)	—19(12)	—9(9)
C(21)	67(9)	47(8)	84(9)	8(8)	—29(9)	—12(7)
O(1)	81(8)	154(10)	72(7)	7(8)	15(7)	—19(7)
O(2)	136(10)	141(9)	97(7)	—24(9)	4(8)	70(7)

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and $U_{ij} = \beta_{ij}/2\pi^2 a_i^{\star} a_j^{\star}$.

ment of the hydrogens yielded the following final unweighted and weighted agreement factors; $R(F) = 0.046$ and $R_w(F) = 0.049$. The function minimized during all the least-squares refinements was $\Sigma w(|F_0| - |F_c|)^2$, where w, the

(Continued on p. 62)

TABLE 6

BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Mo—S	2.478(3)	C(9)—C(10)	1.357(15)
Mo—N(1)	2.233(8)	C(10)—C(11)	1.403(16)
Mo—C(1)	2.349(13)	C(11)—C(12)	1.404(14)
Mo—C(2)	2.419(15)	C(12)—N(1)	1.307(13)
Mo—C(3)	2.383(14)	C(12)—C(13)	1.565(16)
Mo—C(4)	2.320(14)	C(13)—N(2)	1.248(13)
Mo—C(5)	2.268(15)	N(2)—C(14)	1.507(14)
Mo—C(6)	1.929(14)	C(14)—C(15)	1.535(21)
Mo—C(7)	2.011(12)	C(14)—C(16)	1.499(17)
S—C(13)	1.748(10)	C(16)—C(17)	1.411(19)
C(1)—C(2)	1.409(22)	C(17)—C(18)	1.397(19)
C(2)—C(3)	1.388(21)	C(18)—C(19)	1.382(21)
C(3)—C(4)	1.489(21)	C(19)—C(20)	1.379(22)
C(4)—C(5)	1.417(23)	C(20)—C(21)	1.387(19)
C(5)—C(1)	1.415(22)	C(21)—C(16)	1.397(17)
N(1)—C(8)	1.364(13)	C(6)—O(1)	1.164(17)
C(8)—C(9)	1.370(16)	C(7)—O(2)	1.113(15)

TABLE 7

ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

S—Mo—N(1)	76.9(2)
S—Mo—C(7)	75.2(3)
N(1)—Mo—C(6)	81.4(4)
C(6)—Mo—C(7)	76.6(5)
S—Mo—C(6)	121.5(4)
N(1)—Mo—C(7)	127.5(5)
C(2)—C(1)—C(5)	107.8(1.2)
C(1)—C(2)—C(3)	110.5(1.3)
C(2)—C(3)—C(4)	106.2(1.2)
C(3)—C(4)—C(5)	106.6(1.2)
C(4)—C(5)—C(1)	108.7(1.2)
Mo—S—C(13)	105.3(4)
Mo—N(1)—C(8)	117.6(6)
Mo—N(1)—C(12)	124.0(7)
C(8)—N(1)—C(12)	117.1(9)
N(1)—C(8)—C(9)	121.6(1.0)
C(8)—C(9)—C(10)	121.2(1.0)
C(9)—C(10)—C(11)	117.9(1.0)
C(10)—C(11)—C(12)	117.0(1.0)
C(11)—C(12)—N(1)	124.7(1.1)
C(11)—C(12)—C(13)	115.8(9)
N(1)—C(12)—C(13)	119.4(8)
C(12)—C(13)—S	112.4(7)
C(12)—C(13)—N(2)	117.6(9)
S—C(13)—N(2)	130.0(9)
C(13)—N(2)—C(14)	116.4(9)
N(2)—C(14)—C(15)	105.5(1.0)
N(2)—C(14)—C(16)	107.7(9)
C(15)—C(14)—C(16)	113.7(1.0)
C(14)—C(16)—C(17)	122.5(1.1)
C(14)—C(16)—C(21)	120.9(1.1)
C(17)—C(16)—C(21)	116.4(1.1)
C(16)—C(17)—C(18)	120.0(1.2)
C(17)—C(18)—C(19)	122.0(1.2)
C(18)—C(19)—C(20)	118.6(1.3)
C(19)—C(20)—C(21)	119.9(1.2)
C(20)—C(21)—C(16)	123.9(1.2)
Mo—C(6)—O(1)	178.8(1.1)
Mo—C(7)—O(2)	176.2(1.1)

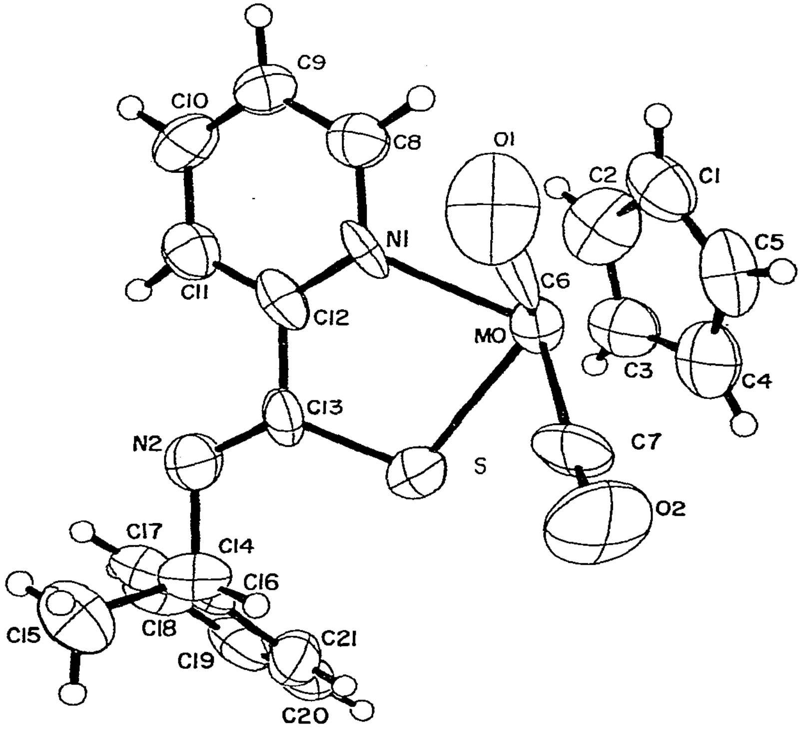

Fig. 1. A general view of the molecule in its correct absolute configuration showing the labelling scheme used in the crystallohraphic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and of convenient size for the hydrogen atoms.

TABLE 8. LEAST SQUARES PLANES (IN ORTHOGONAL Å SPACE) AND DEVIATIONS OF ATOMS FROM THESE PLANES (in Å)

(a) Plane based on C(1), C(2), C(3), C(4) and C(5).

$0.9565x + 0.2881y - 0.0464z = 3.4099$

C(1)	−0.0011	C(2)	0.0124
C(3)	−0.0179	C(4)	0.0170
C(4)	−0.0104	Mo	−2.0068

(b) Plane based on N(1), C(8), C(9), C(10), C(11) and C(12).

$-0.8727x - 0.0309y + 0.4873z = 1.8600$

N(1)	0.0032	C(8)	−0.0254
N(9)	0.0349	C(10)	−0.0226
C(11)	0.0013	C(12)	0.0085
C(13)	0.0881	Mo	−0.3936
S	−0.2732	N(2)	0.4282

(c) Plane based on N(1), S, C(12) and C(13).

$-0.7896x - 0.0568y + 0.6110z = 1.9846$

N(1)	0.0474	S	−0.0331
C(12)	−0.0819	C(13)	0.0676
Mo	−0.0170	C(8)	−0.0508
N(2)	0.2765	C(11)	−0.2986

(d) Plane based on S, N(1), C(6) and C(7).

$0.9570x + 0.2583y - 0.1315z = -0.0624$

S	−0.0575	N(1)	0.0583
C(6)	−0.0700	C(7)	0.0692
Mo	0.9911		

(e) Plane based on C(16), C(17), C(18), C(19), C(20) and C(21).

$0.5999x + 0.7961y - 0.0796z = -1.5320$

C(16)	0.0174	C(17)	−0.0090
C(18)	−0.0012	C(19)	0.0033
C(20)	0.0054	C(21)	−0.0159
C(14)	−0.0311		

(f) Plane based on S, N(2) and C(13).

$-0.7217x + 0.0926y + 0.6859z = 2.3964$

C(12)	0.0631	C(14)	0.0501
Mo	0.4604	N(1)	0.4123

Angles between planes:	Plane 1	Plane 2	Angle
	(c)	(b)	8.67
	(c)	(f)	10.35
	(b)	(f)	16.00

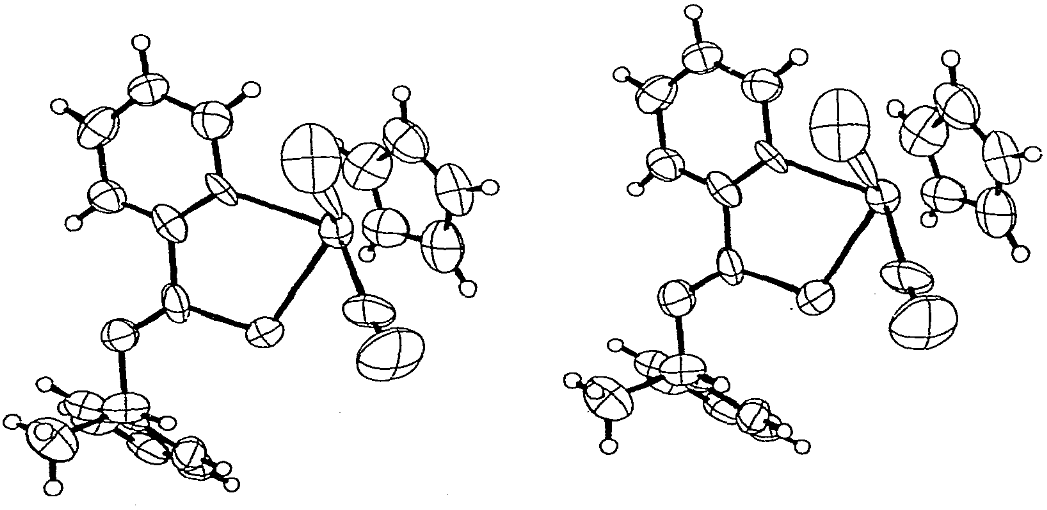

Fig. 2. A stereo pair of the molecule in its correct absolute configuration.

TABLE 9

TORSIONAL ANGLES (°)[a]

Atoms				Angle
A	B	C	D	
Mo	N(1)	C(12)	C(13)	15.47
Mo	S	C(13)	N(2)	—168.91
Mo	S	C(13)	C(12)	8.61
C	C(13)	N(2)	C(14)	2.14
S	C(13)	C(12)	N(1)	—15.58
C(12)	C(13)	N(2)	C(14)	—175.27
C(13)	N(2)	C(14)	C(16)	—102.25
C(13)	N(2)	C(14)	C(15)	135.97

[a] According to the IUPAC-IUB convention [24], i.e., in the fragment ABCD, + = clockwise rotation of bond AB about bond BC so as to eclipse CD with AB along the line of sight (BC).

weighting factors were $[\sigma(|F_o|)]^{-2}$. The atomic scattering curves of Cromer and Mann [13] were used for the nonhydrogen atoms and, for the hydrogen atoms, the curve of Stewart et al. [14] was used. Corrections for the anomalous scattering of Mo and S were made at the end of the refinement and during the calculations associated with the absolute configuration determination. The values used for these corrections were those given by the International Tables for X-ray Crystallography [15]. The estimated standard deviations were computed from the inverse matrix of the final least squares. The standard deviations of the mean were calculated as $[\Sigma(x_i - x)^2/m(m-1)]^{1/2}$. Final positional and thermal parameters are presented in Tables 3—5. Bond lengths and angles are given in Tables 6 and 7. The equations of the least-squares planes through selected groups of atoms and the dihedral angles between them are given in Table 8. Torsional angles are listed in Table 9. The stereo drawings (Figs. 1—3) were obtained with

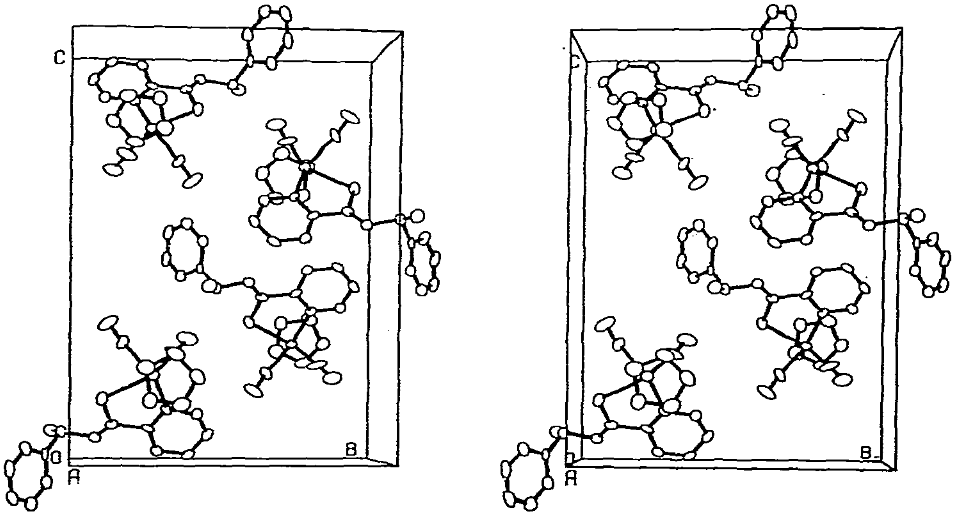

Fig. 3. A packing diagram of the molecules in their correct absolute configuration.

TABLE 10

DETERMINATION OF THE ABSOLUTE CONFIGURATION OF THE DIASTEREOISOMER WITH $(-)_{579}$-$(+)_{436}$

Reflection number	Indices	F(calc) (*hkl*)	F(calc) ($\bar{h}\bar{k}\bar{l}$)	Calculated *F* ratio [a]	Observed *F* ratio [b]
1	1, 7, 1	25.59	27.21	0.94	0.94
2	1, 4, 1	59.77	56.53	1.06	1.08
3	4, 9, 3	25.07	23.92	1.05	1.05
4	1, 3, 3	43.54	45.73	0.95	0.96
5	2, 2, 3	38.75	41.81	0.93	0.94
6	1, 1, 4	39.15	37.69	1.04	1.01
7	3, 3, 5	23.91	25.01	0.96	0.98
8	1, 1, 6	42.24	44.66	0.95	0.95
9	2, 1, 7	17.50	15.93	1.10	1.12
10	6, 2, 10	21.34	20.35	1.05	1.00
11	1, 9, 10	25.27	24.13	1.05	1.05
12	1, 3, 11	25.43	24.22	1.05	1.06
13	4, 2, 12	21.43	20.37	1.05	1.05
14	4, 5, 12	22.46	21.44	1.05	1.04

[a] Calc. *F*(*hkl*)/Calc. *F*($\bar{h}\bar{k}\bar{l}$). [b] Ratio of experimentally measured *F*(*hkl*)/*F*($\bar{h}\bar{k}\bar{l}$).

Johnson's ORTEP 2 [16] and represent the molecule in its correct absolute configuration. A table of observed and calculated structure factors is available as supplementary material *.

Determination of the absolute configuration

When refinement converged, the molecular configuration was that given in Fig. 1—3. A check of *F*(*hkl*) calculated for that absolute configuration and its enantiomer showed 14 reflections suitable for the Bijvoet test [17]. These reflections were measured, each four times, using the diffractometer routine MODE = —1 [18] in the order *hkl*, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$, *hkl*, *hkl*, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$, *hkl*, and the four independently measured values were then averaged. The results are given in Table 10, where it is shown that the coordinates initially chosen and used for Figs. 1—3 correspond to those of the correct enantiomer. The absolute configuration thus obtained shows C(14) (the optically active carbon derived from the parent optically active amine) in an (*S*) configuration which is the known configuration of the amine used in the synthesis of the ligand [10]. Using the extension of the *R*,*S* system [2] to *polyhapto* ligands in organometallic complexes [1], the priority sequence of the ligands is $C_5H_5 > S > N > CO$. Thus. according to the sequence rule of the *R*,*S* system and the line of sight convention given in the Introduction, the configuration at the Mo atom is (*S*). In Fig. 4, which is a double stereo picture (drawn using program BMFIT [19]) comparing the structural characteristics of this molecule with the Schiff base cation I, it was necessary to invert the coordinates of the latter since the absolute configuration of its

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* A table of Structure Factors has been deposited as NAPS document No. 03428 with ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document and remitting $ 5.00 for microfiche and $ 3.00 for photocopies. Advance payment is reuiqred. Make checks payable to Microfiche Publications. Outside the United States or Canada, postage is $ 2.00 for a photocopy or $ 1.00 for a fiche.

TABLE 11

COMPARISON BETWEEN THE MOLECULAR PARAMETERS OF I, II AND V

Compound	Mo—$\overline{\text{C(Cp)}}$ [a]	Mo—Cp	Mo—basal plane	Mo—N	Mo—S	S—C	S—Mo—N or N—Mo—N	CO—Mo—CO	Mo—C(O)	C—O	Reference
I	2.345(25) [c]	2.005	0.948	2.182(19) [b] 2.258(10)	—	—	74.0(4)	73.5(6)	1.984(14) 1.988(14)	1.120(18) 1.136(17)	3
II	2.355(23) [c]	2.012	1.041	2.209(3)	2.514(1)	1.731(4)	63.79(8)	72.8(2)	1.949(5) 1.966(5)	1.151(7) 1.144(7)	4
V	2.348(26)	2.007	0.991	2.233(8)	2.478(8)	1.748(10)	76.9(2)	76.6(5)	1.929(14) 2.011(12)	1.164(17) 1.113(15)	This work

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[a] Mean value and standard deviation of the mean. [b] Mo—N(imine) bond is listed first. [c] Erroneously calculated elsewhere [3,4] as 2.345(14) and 2.355(51), respectively.

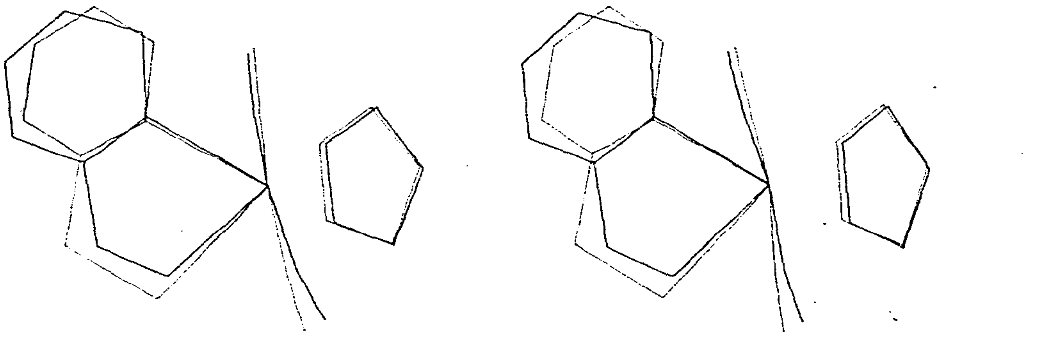

Fig. 4. A double stereo picture of the (η^5-C_5H_5)Mo(CO)$_2$(NN) and (η^5-C_5H_5)Mo(CO)$_2$(NS) moieties of compounds I and V, respectively.

Mo atom is, as previously stated, (*R*). The configuration around the Mo atom of the preferred diastereoisomer is (*S*) for all the three compounds I, II and V. Thus, differences in chemical composition between these compounds such as the size of the chelate ring and the nature of the binding atoms to the metal cause no changes in the CD rotational sign of the 579 nm band.

Description of the structure and discussion

A view of the molecule, in its correct absolute configuration, including the numbering system used in the crystallographic study is given in Fig. 1. The binding atoms of the bidentate ligands are the pyridine nitrogen and the sulfur atom. Thus, the correct structure of the molecule is that described by compound V (see Introduction).

On the assumption that the η^5-C_5H_5(=Cp) ligand is counted as a single binding point to the metal, the coordination polyhedron around the Mo atom can be best described as a distorted square pyramid. The distortion from the theoretical square pyramid geometry around the Mo atom is due to the differences in length between the Mo—S, Mo—N and the two Mo—(CO) bonds (2.478(3), 2.233(8) 1.929(14) and 2.011(12) Å, respectively) and to the fact that the bite of the ligand produces a N—Mo—S angle of only 76.9(2)°. This value of the N—Mo—S ligand angle is close to that of 74.0(4)° observed for the corresponding N—Mo—N angle in I. Both are significantly higher than the value of 63.8(1)° obtained for bite of the thioamide ligand in II where a four-membered chelate ring is produced, as opposed to the five-membered chelate rings of compounds I and V. The slight opening of the ligand angle from 74.0(4) to 76.9(2)° when going from the Schiff base pair of nitrogens in I to the S, N pair in V is probably due to introduction of the longer Mo—S and S—C(13) bonds in V vs. the Mo—N(1) and N(1)—C(16) distances in I. The value of 76.9(2)° obtained for V compares well with the corresponding angles of 78.18(6) and 79.00(7)° observed by Yamanouch and Enemark [20] for a similar five-membered chelate ring. Interestingly, the C—Mo—C angle defined by the two carbonyl ligands remains largely undisturbed when going from the four-membered chelate ring in II, to the five-membered rings of I and V. The Mo atom lies 2.007 Å from the plane of the Cp ring (see Table 8). The Mo—C(Cp) distances range from 2.268(15) to

2.419(15) Å, with an average of 2.348(26) Å. The C—C distances of the Cp ring range from 1.398(21) to 1.489(21) Å. The internal angles of the five-membered ring range from 106.2(1.2) to 110.5(1.3)°, with an average of 108°, as expected. Thus, as can be seen from Table 11, the geometry of the Mo—(η^5-C_5H_5) fragment of compound V compares well with that of I and II. These similarities in the Mo—(η^5-C_5H_5) fragments of I and V are best seen in the dual stereo plot (Fig. 4), which was drawn having the Mo, carbonyl carbons and pyridine nitrogen as common atoms. For all three compounds, the range of the Mo—C(Cp) and Cp(C—C) distances reflect the ability of the Cp fragment to undergo librational motion around the Mo—(Cp ring centroid) vector. This phenomenon has been previously documented [21] and is thus not repeated here. However, the variations in the Mo—C(Cp) distances seem to be mirrored in the Cp(C—C) bonds i.e., the carbon atoms which are more loosely bonded to the Mo are more tightly bonded to each other. The same pattern was observed for compounds I and II and by others [22].

The Mo—C(CO) distances in V are 1.929(14) and 2.011(12) Å, while the corresponding C—O distances are 1.164(17) and 1.113(15) Å, respectively. As might be expected, the shorter C—O bond is associated with the longer Mo—C(CO) distance. The difference of 0.082 Å between the two Mo—C(CO) distances is significant and may be the result of the "*trans*" effect, although that effect was not observed for compound II. The two Mo—(CO) distances in I are equal, within their estimated standard deviations, as expected, since the two nitrogen ligands are quite similar in nature. As usual with metal carbonyl fragments, the Mo—C—O angles deviate slightly from linearity. The value of 2.233(8) Å observed for the Mo—N bond of compound V is identical (within 3 σ) with the corresponding value of 2.258(11) Å found for compound I.

Bernal et al. [4] in comparing the molecular parameters of various molybdenum compounds containing sulfur, nitrogen, carbonyl and Cp ligands observed that when the ligand angle S—Mo—N or S—Mo—S opens up and the S—C(ligand) distance is long, there is a short Mo—S distance. The same pattern is found in compound V when compared to II. Thus, an opening up of the ligand angle from 63.8(1) to 76.9(2)° and a lengthening of the S—C(ligand) bond from 1.731(4) to 1.748(6) when going from compound II to V leads to a significantly shorter Mo—S distance (2.514(1) vs. 2.478(8) Å). It seems that the shorter Mo—S distance of compound V when compared to the corresponding bond in II reflects the better ability of the sulfur and molybdenum electrons to interact in the five-membered chelate ring than in the four-membered system. Concomitantly, there is a lengthening of the S—C bond in V as compared to II. According to Hordvik [23], a distance of 1.72 Å represents a π order of 0.56 for a S(II)—C(sp^2) system while a bond length of 1.75 Å (as observed for V) corresponds to a π bond order of 0.47. The value of 1.248(13) Å observed for the N(2)—C(13) distance in compound V corresponds to a C—N double bond.

An important structural difference between compounds I and V is that, whereas in I the Mo atom, the pyridine ring and ligand plane are coplanar, in compound V the pyridine ring makes an angle of 8.7° with the plane defined by the Mo chelate ring. This difference is best appreciated by reference to the double stereo plot (Fig. 4). Quantitatively, this can be expressed as follows: the torsional angle for the S, C(13), C(12), N(1) fragment of compound

V is —15.58° (see Table 9), while for II it is nearly zero. This distortion from planarity in V is probably caused by the need to preserve a common geometry for the CpMo(CO)$_2$N(pyridine) fragment while trying to accomodate the much larger Mo—S and S—C bonds present in V. The easiest way to accomodate these longer bonds seems to be an out of plane movement of the sulfur atom.

Although the average value of the two C—N bonds (1.336 Å) is virtually identical to the values found for the free pyridine molecule (1.340 Å) [26], bonds N(1)—C(8) and N(1)—C(12) differ significantly (1.364(13) and 1.307(13) Å, respectively). This shortening of the N(1)—C(12) bond may be due to its being part of plane c (see Table 8) but cannot be the result of conjugation with the N(2)—C(13) double bond since the C(12)—C(13) distance is 1.565(16) Å.

In the present structure, H(14) was located, by least-squares refinement, at an H---S distance of 2.52(7) Å, which is significantly smaller than the sum of the Van der Waals radii (3.05 Å) [25]. Such short H---S distances, which were also observed by others [27], indicate a significant interaction between the sulfur and the hydrogen atoms, although it seems to us that the position of H(14) is essentially determined by steric considerations of the entire phenylamine group, as described in the next chapter. No other unusual intramolecular or intermolecular contacts were found.

Stereochemical considerations and conformations which the molecule can acquire

The conformation found in the crystal is such that the phenyl ring projects towards the cyclopentadienyl ring and the methyl group points to the opposite side of the (η^5-C_5H_5) ring. The hydrogen atom H(14), bonded to the asymmetric carbon C(14) forms a C(14)—H(14) vector which is almost in the ligand plane (defined by N(1), S, C(12), C(13) and containing also the Mo atom). This conformation is similar to that found for compound II but differs from that observed for I where the phenyl ring projects out of the complex, opposite the cyclopentadienyl ring. However, we note that whereas structures II and V correspond to the preferred diastereoisomer, compound I represents the non-preferred species. We are presently investigating the possibility that the relative position of the phenyl and Cp rings is dependent on diastereoisomer preference. In a fluid medium, molecule V could prefer conformations which are different from that found in the crystal. Two major sources for different conformations within the molecule can be envisaged; first, the conformers that arise from rotation of the (*S*)-α-phenylethyl group around the C(14)—N(2) bond; second, the conformers that arise from rotation of the phenyl ring around the C(14)—C(16) vector. As the chiral carbon atom C(14) attempts to rotate around the N(2)—C(14) bond its substituents, the large phenyl ring, the middle size methyl group and the small hydrogen H(14), give rise to various degrees of crowding with adjacent groups. Thus, such a rotation would bring the methyl group C(15) into the ligand plane, in which case C(15) and the sulfur atom would come as close as 2.3 Å. Also, the freely rotating hydrogen atoms of the methyl would be as close as 1 Å to the sulfur atom. An opposite rotation would produce short contacts, first between the phenyl and cyclopentadienyl hydrogens and then between C(17) and the sulfur atom. A rotation of the phenyl group around the C(14)—C(16) vector, at this position, would result in bad contacts between the phenyl and methyl hydrogens and also between O(2) and the phenyl ring. Thus, all the conformations in which H(14) is either in the ligand plane, pointing towards the Mo atom or at angles of up to ±40° with respect to this plane seem to be acceptable. Rotation of the phenyl plane around the C(14)—C(16) vector causes bad interatomic contacts between the phenyl hydrogens in the *ortho* position and the methyl hydrogens. Finally, further rotation produces short contacts between the phenyl ring *ortho* hydrogens and the sulfur atom. In addition to the two major sources for different conformations already mentioned, rotations around the C(13)—N(2) vector may also be considered. However, because of the double bond nature of the C(13)—N(2) bond (1.248(13) Å), the barrier to such a rotation should be high. Consequently, the conformation found in the crystal appears to be the most favorable one (if the chiral carbon is (*S*)) and thus represents a sensible choice for both, solid and solution. In other words, the most favorable conformation is dictated mainly by intramolecular steric needs and not by intermolecular packing forces.

Acknowledgments

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