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**Supplementary Material Available:** A listing of crystal structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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## Absolute Configurations of Organometallic Compounds. 3.<sup>1</sup> Structure and Absolute Configuration of the Square-Pyramidal Complex [(+)<sub>579</sub>-(C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>2</sub>(NN\*)]PF<sub>6</sub> (NN\* = Schiff Base Derived from Pyridine-2-carbaldehyde and (S)-(-)-α-Phenylethylamine)

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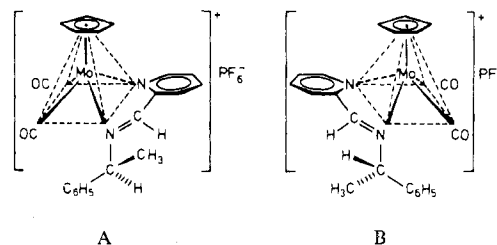
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The structure of (+)<sub>579</sub>-[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>(NN\*)]PF<sub>6</sub> with NN\* = the Schiff base derived from pyridine-2-carbaldehyde and (S)-(-)-α-phenylethylamine was determined using standard single-crystal x-ray diffraction methods. The absolute configuration was determined by refinement of the data using the anomalous scattering contributions of Mo and P to a final  $R(F) = 0.056$  for 2634 independent reflections having  $I > 3\sigma(I)$ . The substance crystallizes in the space group  $P2_12_12_1$  with unit cell dimensions of  $a = 12.249$  (4),  $b = 9.236$  (3), and  $c = 20.692$  (9) Å and  $Z = 4$  molecules/unit cell. The square-pyramidal coordination of the Mo atom is defined by two carbonyl carbons and two Schiff base nitrogens occupying the four basal plane sites and the five carbons of the η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> ligand in the axial position. The Mo-ligand distances and the bond lengths and angles within the ligands are normal and compare closely with those of recent structure determinations of comparable precision. The Mo atom is 0.95 Å above the plane formed by the four basal plane ligands. The conformation of the (S)-α-phenylethyl group with respect to the ligand plane, defined by the pyridine ring, the imine system, and the Mo atom, is discussed. The configuration at the metal atom in the (+)<sub>579</sub> isomer is specified as (S). The PF<sub>6</sub><sup>-</sup> anion executes large amplitude torsional motion in the lattice, as is commonly the case for this anion when not hydrogen bonded.

### Introduction

In the last 7 years, optically active organometallic compounds became available in which a transition element is the chiral center.<sup>3,4</sup> These stereochemically labeled compounds were used to elucidate the steric course of reactions.<sup>5</sup> For correlation of configuration, chiroptical and chemical methods had to be applied as the absolute configurations of all these compounds were not known. In a preliminary communication, we published the first determination of the absolute configuration of such a compound.<sup>6</sup> Meanwhile the determination of the absolute configurations of other optically active organometallic complexes has been announced.<sup>2,7-9</sup> Here we report the details of our x-ray diffraction study on the compound (+)<sub>579</sub>-[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>(NN\*)]PF<sub>6</sub> with NN\* = Schiff base derived from pyridine-2-carbaldehyde and (S)-(-)-α-phenylethylamine.

In the reaction of C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Cl with the Schiff base NN\* one of the carbonyl ligands and the covalently bound chlorine substituent are displaced by NN\*, and in a metathetical reaction the anion Cl<sup>-</sup> can be replaced by PF<sub>6</sub><sup>-</sup>.<sup>10,11</sup> On substitution of CO and Cl<sup>-</sup> in C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Cl by NN\*, a new asymmetric center at the Mo atom is formed. Therefore using the (S)-(-)-α-phenylethyl group in the amine part of the Schiff base NN\*, two diastereoisomers A and B arise



which differ only in the configuration at the metal atom.<sup>10,11</sup> Both isomers A and B show different <sup>1</sup>H NMR spectra and can be separated by fractional crystallization.<sup>11</sup>

Compounds A and B are configurationally stable in the solid state and in solution at low temperatures. At 75 °C in DMF solution the two diastereoisomers A and B interconvert by what seems to be an intramolecular metal-centered rearrangement, probably taking place by a 180° rotation of the chelate ligand NN\* with respect to the metal atom.<sup>5,12-14</sup> In the equilibrium at 75 °C, which in DMF is approached in a first-order reaction with a half-life of 26.3 min,<sup>12</sup> the isomer ratio is A/B = 40/60. This isomer ratio is a measure of the optical induction of the S-configured asymmetric carbon atom in the Schiff base NN\* on the formation of the two different configurations at the Mo atom in the equilibrium.<sup>15</sup> The asymmetric induction at the metal atom in the compounds C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>LL\* is strongly dependent on the nature of the chelate ligand LL\*.<sup>15</sup>

In the asymmetric hydrogenation of suitably substituted olefins and similar reactions the best optical yields are obtained

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Table I. Crystal Data

Chemical formula	(C <sub>21</sub> H <sub>19</sub> MoN <sub>2</sub> O <sub>2</sub> )PF <sub>6</sub>
Mol wt	572.28
Crystal shape	Diamond-shaped parallelepiped
Approx crystal dimensions	0.20 × 0.40 × 0.40 mm along the edges
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell data	a = 12.249 (4) Å b = 9.236 (3) Å c = 20.692 (9) Å V = 2340.92 Å <sup>3</sup>
Density (measd)	1.62 (2) g cm <sup>-3</sup>
(calcd)	1.62 g cm <sup>-3</sup>
Radiation used	Mo Kα (0.71069 Å)
Linear absorption coefficient	μ = 6.93 cm <sup>-1</sup>
No. of data used in refinement	2634

with Rh catalysts containing chelating diphosphines with optically active centers either at the phosphorus atom or in the chelate ring.<sup>16-24</sup> In many of the catalytic species the Rh atom also bonded to olefin, hydrogen, solvent, and so on, is an asymmetric center, and the possible diastereoisomers probably are interconverting rapidly. The optical induction of the chelate centers on the Rh center could be one of the major factors responsible for the optical yield in the products. The compounds C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>LL\* can be used as models for the study of problems like epimerization and optical induction at the metal atom. From the x-ray determination of isomer A, we wanted to obtain information about the relationship of the optically active centers in the chelate ring and on the metal atom.

### Experimental Section

Crystals suitable for x-ray diffraction were grown from a solvent mixture of acetone/methylene chloride/ethanol in the ratio 20:3:1. The crystal chosen for this study was a diamond-shaped plate whose six faces were (110), (110), (110), (110), (001), and (001). The dimensions of the crystal listed in Table I were the lengths along the edges of the plate and the thickness, respectively, the latter being along the *c* direction of the crystal. We did not correct the diffracted intensities for absorption. The space group and a set of approximate cell constants were obtained from data collected on films.

The data crystal was mounted on an automated Picker diffractometer and manually centered. Accurate cell constants and an orientation matrix were obtained from the automatic centering of 30 high-angle reflections using Mo Kα radiation and a high-density graphite monochromator. A summary of crystal and intensity data collection is given in Table I. The latter were measured at 21 °C using the  $\theta$ - $2\theta$  method, and the length of the scan was determined by the expression

$$\text{scan length} = 1.80(1.0 + 1.0 \tan \theta)$$

with the center of the scanning set at the unweighted average value of the Bragg angle corresponding to Mo Kα<sub>1</sub> and Mo Kα<sub>2</sub> wavelengths (0.7104 Å). In order to avoid problems associated with partial resolution of the α<sub>1</sub> and α<sub>2</sub> peaks, background was taken to be the first and last five points of the scan. Two standard reflections (0,1,10 and 3,2,17) were monitored every 30 data points in order to check on electronic stability and the possibility of crystal decay. There was no significant change in the standards during the entire period of data collection. The data were not smoothed (i.e., they were not fitted to a polynomial) and over the range of 0 ≤ 2θ ≤ 41.6°, a set of *hkl* and of *hkl* was collected in order to have large numbers of Friedel pairs available for the determination of the absolute configuration. The structure was solved and refined using the data from 0 ≤ 2θ ≤ 41.6° without the introduction of anomalous scattering and using standard Patterson, Fourier, and least-squares methods.<sup>25</sup>

During the initial stages of this study (i.e., at the time of our preliminary report<sup>6</sup>) the following programs were used for the processing of the data: PROCH (initial processing of the raw data); DATAPH (Lorentz-polarization correction); ECSORTH (sorting and averaging); JIMDAP (a local version of the Fourier summation program originally written by A. Zalkin); LINUS (a version of Busing, Martin, and Levy's least-squares program); ORFFE (the function and error

program); ORTEP-2 (C. Johnson's molecular plotting program; used throughout). The present report used the output of ECSORTH and the results of the earlier<sup>6</sup> report to finish the refinement. All these subsequent calculations were done using the X-Ray 72 system of crystallographic programs. The refinement of the data was carried out using unit weights and with the inclusion of hydrogen atoms located at computed, idealized positions which we recomputed after each group of cycles of heavy-atom refinements. Each hydrogen was assigned the isotropic thermal parameter of the heavy atom to which it is attached. This procedure was not used for H8 (that hydrogen attached to the chiral carbon) since we wanted to investigate the possibility that this important hydrogen would refine as an independent atom. This turned out to be the case and is the reason that the positional and isotropic thermal parameters for this hydrogen (alone) appear with errors in Table II. The final discrepancy factor for the refinement is

$$R(F) = \Sigma(|F_o| - |F_c|) / \Sigma|F_o| = 0.056$$

There is considerable thermal motion in the PF<sub>6</sub><sup>-</sup> ion in the lattice as is generally the case for groups like PF<sub>6</sub><sup>-</sup>,<sup>26</sup> BF<sub>4</sub><sup>-</sup>,<sup>27,28</sup> ClO<sub>4</sub><sup>-</sup>,<sup>29</sup> and related ions found in nonhydrogen bonded lattices. This can readily be observed in the values of the thermal parameters in Table II as well as in the size and shapes of the thermal ellipsoids shown in Figure 2. A final difference electron density map showed only low-density random noise at chemically unlikely locations. The final positional and thermal parameters are listed in Table II. Distances and angles, together with their estimated standard deviations, are given in Table III. The equations of relevant least-squares planes and deviations of atoms from such planes are listed in Table IV. Finally, a comparison of molecularly important parameters associated with our cation is made in Table V. A table of the structure factors, their estimated standard deviations, and the calculated structure factors is available as supplementary material.

### Determination of the Absolute Configuration

As mentioned earlier, a group of *hkl* reflections were measured in order to compare them with their *hkl* counterparts for the determination of absolute configuration. There are many pairs which differ significantly and a comparison of  $F(hkl)/F(hkl)_{\text{obsd}}$  vs.  $F(hkl)/F(hkl)_{\text{calcd}}$  agrees for 38 reflections when the absolute configuration of the cation is that shown in Figure 1. For the calculation of  $F(hkl)$  and  $F(hkl)$ , the anomalous contribution to the scattering curves of Mo and P given in ref 30 was used to correct the curves of Cromer and Mann.<sup>31</sup> The absolute configuration thus obtained shows C8 (the optically active carbon derived from the parent optically active amine) in an *S* configuration which is the known configuration<sup>25</sup> for the amine used in the synthesis of the Schiff base.

### Discussion

**Description of the Structure.** Figure 1 gives a convenient stereoview of the molecule, as well as the numbering system used in the crystallographic study. On the assumption that the η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> = Cp ligand can be counted as a single binding point to the metal, the coordination polyhedron around the Mo atom is square pyramidal. Distortions from this geometry are due to the differences in length between the Mo-N and Mo-C(O) bonds (av Mo-N = 2.220; av Mo-C = 1.968 Å). The molybdenum atom is out of the plane of the two nitrogen and two carbonyl carbons by 0.948 Å and out of the plane of the Cp ring by 2.005 Å (see details of planes in Table IV). However, if a plane is defined by the pyridine atoms (N2, C17, ..., C21) all its atoms lie in that plane (maximum deviation, C18 = 0.012 Å). At the same time, the imine carbon and nitrogen lie in this plane with very minor, if not negligible, deviations (C16 = 0.048 and N1 = 0.007 Å). Carbon 8 deviates a little more (0.173 Å), which corresponds to an angular displacement of 2.02° from that plane and which may be the result of packing and/or the result of steric crowding between H9(1) and H16, as discussed below. C8 is also out of the plane of the phenyl ring by approximately the same amount. We surmise that packing forces against the large surface of the phenyl ring cause the pivoting point (C8) to buckle a little from both planes. Except for this small deviation

Table II. Positional and Thermal Parameters<sup>a</sup> with Estimated Standard Deviations in Parentheses

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Mo	15101 (8)	01312 (11)	31088 (5)	330 (8)	319 (8)	376 (8)	9 (5)	-3 (5)	13 (5)
O1	0720 (9)	3973 (14)	1403 (7)	445 (61)	838 (88)	1091 (95)	134 (66)	160 (67)	-53 (81)
O2	-0251 (8)	0697 (12)	2050 (5)	518 (61)	756 (74)	738 (72)	74 (59)	-224 (56)	17 (62)
N1	2448 (8)	-1015 (11)	2373 (5)	374 (55)	344 (52)	339 (51)	-19 (50)	-23 (47)	10 (44)
N2	2108 (9)	-1923 (11)	3583 (5)	395 (59)	364 (53)	423 (57)	-27 (52)	-38 (54)	60 (48)
C1	0098 (11)	-0647 (14)	3426 (7)	385 (71)	528 (81)	632 (87)	-14 (69)	28 (69)	-29 (73)
C2	0431 (11)	0447 (15)	2406 (7)	405 (68)	451 (76)	564 (77)	-20 (65)	9 (65)	-31 (65)
C3	1707 (13)	1778 (16)	3959 (7)	625 (98)	492 (76)	539 (79)	-17 (80)	148 (76)	-133 (66)
C4	2988 (11)	1819 (14)	3144 (8)	421 (69)	428 (66)	602 (81)	-107 (62)	22 (77)	-77 (77)
C5	1232 (12)	2464 (15)	3421 (8)	498 (89)	356 (66)	697 (93)	18 (66)	124 (75)	-27 (68)
C6	2806 (12)	1386 (16)	3783 (7)	523 (87)	473 (77)	589 (86)	-39 (75)	-140 (79)	-87 (71)
C7	2020 (13)	2501 (14)	2910 (7)	590 (88)	320 (61)	690 (96)	-68 (69)	-46 (80)	89 (63)
C8	2719 (11)	-0384 (14)	1732 (6)	554 (78)	388 (67)	357 (60)	47 (64)	49 (59)	42 (52)
C9	3904 (12)	-0627 (17)	1527 (7)	523 (86)	607 (92)	551 (82)	-43 (76)	42 (72)	100 (75)
C10	1915 (12)	-0893 (17)	1213 (6)	487 (77)	615 (86)	301 (58)	136 (74)	15 (59)	81 (62)
C11	1815 (13)	-2324 (17)	1041 (7)	592 (99)	578 (88)	477 (79)	-19 (78)	-76 (73)	72 (70)
C12	1351 (14)	0122 (20)	0852 (7)	818 (113)	767 (102)	505 (73)	337 (120)	98 (80)	132 (84)
C13	1149 (15)	-2700 (21)	0538 (7)	754 (118)	983 (135)	398 (75)	-182 (109)	51 (81)	-79 (88)
C14	0678 (16)	-0329 (27)	0341 (8)	688 (111)	1216 (178)	449 (81)	211 (138)	-97 (82)	283 (112)
C15	0584 (16)	-1706 (27)	0197 (7)	699 (120)	1351 (186)	288 (68)	-115 (140)	-60 (80)	92 (102)
C16	2883 (11)	-2206 (13)	2538 (6)	402 (67)	370 (61)	338 (59)	-8 (61)	-13 (59)	-14 (52)
C17	2702 (10)	-2766 (13)	3175 (6)	336 (60)	361 (56)	401 (63)	-16 (53)	-52 (61)	31 (57)
C18	1912 (14)	-2312 (17)	4238 (8)	694 (100)	603 (90)	884 (115)	-248 (83)	-405 (93)	480 (87)
C19	2364 (15)	-3692 (18)	4403 (8)	782 (115)	542 (87)	540 (87)	-83 (92)	-120 (89)	138 (77)
C20	2971 (15)	-4556 (15)	3984 (7)	847 (112)	371 (70)	557 (83)	45 (78)	-135 (85)	138 (63)
C21	3143 (12)	-4089 (15)	3354 (7)	561 (86)	389 (64)	467 (71)	-2 (67)	-75 (65)	20 (57)
P	4164 (3)	4134 (4)	1449 (2)	531 (23)	496 (21)	393 (19)	-54 (19)	38 (17)	25 (17)
F1	3774 (11)	4951 (19)	0845 (5)	1392 (116)	1826 (135)	915 (75)	543 (132)	381 (78)	769 (98)
F2	3121 (8)	4681 (11)	1841 (5)	822 (63)	866 (67)	724 (55)	9 (57)	213 (52)	48 (64)
F3	5181 (11)	3634 (15)	1055 (6)	1121 (95)	1302 (107)	1126 (93)	577 (92)	643 (82)	391 (87)
F4	3483 (16)	2858 (15)	1184 (9)	1710 (144)	1032 (96)	2078 (167)	-559 (122)	269 (151)	-692 (109)
F5	4522 (13)	3201 (23)	2025 (6)	1396 (122)	2819 (214)	800 (82)	1003 (146)	164 (87)	793 (117)
F6	4776 (13)	5465 (19)	1675 (12)	1188 (116)	1693 (167)	3695 (290)	-842 (121)	571 (161)	-1468 (193)

Atom	x	y	z	U, Å <sup>2</sup>	Atom	x	y	z	U, Å <sup>2</sup>
H3	1360	1602	4361	380	H12	1398	1128	0969	507
H4	3642	1687	2903	481	H13	1071	-3691	0429	633
H5	0520	2854	3397	507	H14	0303	0397	0086	760
H6	3319	0905	4057	253	H15	0112	-1960	-0145	760
H7	1919	2906	2490	507	H16	3329	-2719	2240	507
H8	267 (10)	053 (13)	167 (5)	447 (397)	H18	1540	-1734	4532	887
H9-1	4037	-1693	1501	887	H19	2244	-4045	4834	887
H9-2	4023	-0182	1090	887	H20	3266	-5451	4123	887
H9-3	4401	-0177	1847	887	H21	3548	-4655	3058	760
H11	2190	-3037	1269	253					

<sup>a</sup> The positional parameters of Mo were multiplied by 10<sup>5</sup>; those of the other atoms (except H8, ×10<sup>3</sup>) were multiplied by 10<sup>4</sup>. The U<sub>ij</sub> values of all atoms were multiplied by 10<sup>4</sup>.

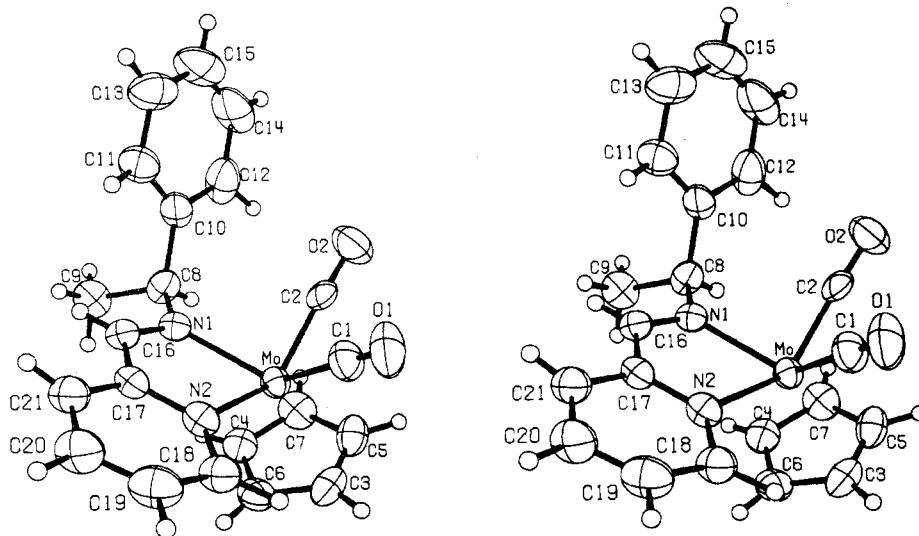


Figure 1. A stereoview of the cation of A in its correct absolute configuration, showing also the numbering system employed in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and are of convenient (arbitrary) size for the hydrogens.

at C8 from planarity, the Mo atom plus the Schiff base ligand atoms, up to the chiral carbon (C8), lie in the plane defined

by the pyridine ring. The methyl carbon (C9) and the phenyl ring are, obviously, out of this plane since C8 is tetrahedral.

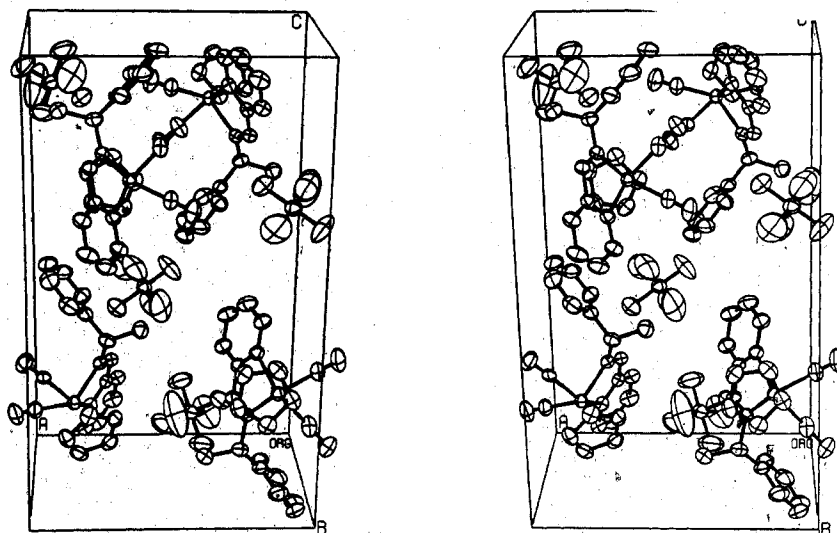


Figure 2. A packing diagram in stereo showing the cation (in its correct absolute configuration) and the anion and their relative locations in the unit cell.

Table III. Bond Distances (Å) and Angles (deg)<sup>a</sup>

(A) Bond Distances			
Mo-N1	2.182 (10)	C10-C11	1.374 (22)
Mo-N2	2.258 (11)	C10-C12	1.384 (22)
Mo-C1	1.984 (14)	C11-C13	1.368 (22)
Mo-C2	1.988 (14)	C12-C14	1.404 (24)
Mo-C3	2.338 (14)	C13-C15	1.349 (28)
Mo-C4	2.390 (14)	C14-C15	1.312 (35)
Mo-C5	2.275 (14)	N1-C16	1.270 (16)
Mo-C6	2.410 (15)	C16-C17	1.433 (17)
Mo-C7	2.313 (14)	C17-C21	1.387 (18)
C1-O1	1.120 (18)	C17-N2	1.359 (16)
C2-O2	1.136 (17)	N2-C18	1.423 (20)
C3-C5	1.406 (21)	C18-C19	1.431 (23)
C3-C6	1.441 (22)	C19-C20	1.394 (23)
C4-C6	1.398 (22)	C20-C21	1.389 (20)
C4-C7	1.428 (20)	P-F1	1.536 (14)
C5-C7	1.432 (22)	P-F2	1.595 (10)
C8-C9	1.529 (20)	P-F3	1.558 (14)
C8-C10	1.530 (19)	P-F4	1.544 (16)
C8-H8	0.85 (12)	P-F5	1.535 (16)
C8-N1	1.486 (15)	P-F6	1.515 (18)
(B) Bond Angles			
N1-Mo-N2	74.0 (4)	C13-C15-C14	120 (2)
N1-Mo-C1	120.9 (5)	C8-N1-C16	119 (1)
N1-Mo-C2	84.8 (5)	C8-N1-Mo	123.4 (8)
N2-Mo-C1	80.5 (5)	N1-C16-C17	120 (1)
N2-Mo-C2	131.1 (5)	C16-C17-N2	117 (1)
C1-Mo-C2	73.5 (6)	C16-C17-C21	120 (1)
Mo-C1-O1	177 (1)	C17-N2-C18	123 (1)
Mo-C2-O2	173 (1)	C17-C21-C20	118 (1)
C6-C3-C5	107 (1)	N2-C18-C19	113 (1)
C6-C4-C7	108 (1)	C18-C19-C20	125 (1)
C3-C5-C7	108 (1)	C19-C20-C21	119 (1)
C3-C6-C4	108 (1)	F1-P-F2	90.5 (6)
C4-C7-C5	107 (1)	F1-P-F3	88.2 (7)
N1-C8-C9	114 (1)	F1-P-F4	85.3 (9)
N1-C8-C10	111 (1)	F1-P-F6	90 (1)
N1-C8-H8	120 (7)	F1-P-F5	175.2 (9)
C9-C8-C10	112 (1)	F2-P-F3	178.6 (7)
C9-C8-H8	100 (8)	F2-P-F4	89.4 (8)
C10-C8-H8	99 (8)	F2-P-F5	90.7 (6)
C8-C10-C11	122 (1)	F2-P-F6	88.9 (8)
C8-C10-C12	119 (1)	F3-P-F4	91.2 (9)
C10-C11-C13	120 (1)	F3-P-F5	90.6 (8)
C10-C12-C14	120 (2)	F4-P-F5	90 (1)
C11-C13-C15	122 (2)	F4-P-F6	175 (1)
C12-C14-C15	121 (2)	F5-P-F6	94 (1)

<sup>a</sup> Estimated standard deviations are in parentheses.

Table V was prepared for the purpose of comparisons with recent literature values from relevant molecules for which the

Table IV. Equations of Least-Squares Planes<sup>a</sup> and Deviations of Selected Atoms from Those Planes (in Å)

(a) Plane Defined by C3, C4, C5, C6, C7		
$4.05515x + 8.16979y + 6.79864z = 4.83851$		
Mo = -2.005	C5 = 0.000	
C3 = -0.002	C6 = 0.003	
C4 = -0.004	C7 = 0.002	
(b) Plane Defined by N2, C17, C18, C19, C20, C21		
$10.29916x + 4.23983y + 5.93597z = 3.49196$		
N2 = -0.010	C19 = -0.008	N1 = 0.007
C17 = 0.002	C20 = 0.001	C16 = 0.048
C18 = 0.012	C21 = 0.002	Mo = -0.036
		C8 = 0.173
(c) Plane Defined by C10, C11, C12, C13, C14, C15		
$-9.45096x - 0.78923y + 13.04380z = -0.16797$		
C10 = 0.011	C14 = -0.001	
C11 = -0.006	C15 = 0.007	
C12 = -0.008	C8 = -0.112	
C13 = -0.003	H8 = -0.216	
(d) Plane Defined by N1, N2, C1, C2		
$4.93389x + 7.61255y + 8.23543z = 2.45681$		
N1 = -0.068	C1 = -0.079	
N2 = 0.070	C2 = 0.077	
Mo = 0.948		

<sup>a</sup> These equations are in direct space and have the form  $px + qy + rz = s$ .

structural studies were comparable with, or better than, ours. The Mo-C(Cp) distances are normal in the sense that they agree closely with the chosen examples. The small differences observed are no doubt due to the variations in ligands opposite the Cp ring; however, it is clear that these variations in ligands produce very small changes in the Cp-Mo fragment. Note for example that the highly accurate (and precise) study of Peterson, Dahl, and Williams<sup>39</sup> (carried out by x-ray and neutron diffraction) gives exactly the same average value for the mean of the Mo-C distance (i.e., they are within one standard deviation from the mean). On the other hand, their compound contains a bridging hydride and a bridging diphenylphosphine while ours contains two nitrogens.

There are definite trends in the Mo-C(CO) distances for the compounds containing N ligands. For example, as the Mo-N distance in compounds I, II, and III increases, one observes a parallel decrease in the Mo-C(CO) distances. When there is a drastic change in the nature of the nitrogen atom (as in the NCO of compound VI) there is also a comparably major change in the carbonyl Mo-C distance. The

Table V. A Comparison of Molecular Parameters with Recent Literature Values (Distances in Å; Angles in deg)

Compd	Mo-N	Mo-C(O)	C-O	Mo-C-O	Mo-C(Cp) <sup>a</sup>	Ref
[C <sub>21</sub> H <sub>19</sub> MoN <sub>2</sub> O <sub>2</sub> ]PF <sub>6</sub> (I)	2.182 (10)	1.984 (14)	1.120 (18)	177 (1)	2.345 (13)	This study
HB(pz) <sub>3</sub> Mo(CO) <sub>2</sub> NNC <sub>6</sub> H <sub>5</sub> (II)	2.258 (11)	1.988 (14)	1.136 (17)	173 (1)		32
	2.231 (5)	1.973 (6)	1.134 (8)	176.34 (15)		
	2.212 (4)	2.020 (6)	1.132 (8)	179.05 (62)		
[(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )(C <sub>5</sub> H <sub>5</sub> N)Mo(CO) <sub>3</sub> ] (III)	2.210 (4)					33
	2.235 (7)	1.965 (8)	1.145 (11)	177.2 (7)		
[(η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> )Mo(CO) <sub>3</sub> ]BF <sub>4</sub> (IV)	2.311 (9)	1.964 (14)	1.092 (18)	177.7 (1.3)		27
		2.029 (10)	1.137 (12)	178 (1)		
		2.036 (10)	1.120 (12)	176 (1)		
(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Mo(CO) <sub>3</sub> (PPh <sub>3</sub> )[(NC) <sub>2</sub> -CC(CN) <sub>2</sub> (CH <sub>3</sub> )] (V)		2.032 (13)	1.130 (15)	177 (1)		34
		1.973 (3)	1.141 (4)	175.5 (3)	2.332 (23)	
(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )Mo(NCO)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (VI)	2.127 (8)	1.934 (10)	1.147 (13)	176.3 (8)	2.297 (33)	35
[Mo(=N=NH <sub>2</sub> )F(Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ]-BF <sub>4</sub> ·CH <sub>2</sub> Cl <sub>2</sub> (VII)	1.762 (12)					36
Mo <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub> ·2(NC <sub>5</sub> H <sub>5</sub> ) (VIII)	2.548 (8)					37
Mo <sub>2</sub> O <sub>2</sub> S <sub>2</sub> (histidine) <sub>2</sub> (IX)	2.257 (7)					
	2.272 (9)					
	2.245 (7)					
	2.237 (8)					
(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Mo <sub>2</sub> (CO) <sub>4</sub> [P(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> H (IX)		1.964 (3)	1.151 (3)	177.9 (2)	2.332 (48)	
		1.964 (3)	1.153 (3)	177.5 (2)		
		1.955 (3)	1.158 (3)	177.2 (2)		
		1.959 (3)	1.149 (3)	178.0 (2)		

<sup>a</sup> Mean and standard deviation from mean in parentheses.

variations in the CO distances are very small and of doubtful significance for the cases listed in Table V, and the Mo-C-O angle changes in an equally small and, apparently, erratic manner. However, there are small deviations from linearity as is usually the case with metal-carbonyl fragments. There is a clear variation in Mo-C(CO) distance upon complexation with  $\pi$ -arene ligands, a fact that has already been noted by Clark and Palenik<sup>27</sup> in the example quoted in Table V. That is, the Mo-C(CO) distance is distinctly greater than 2.00 Å while with ligands, such as those in the other examples, the value is less than 2.00 Å. Finally, the Mo-N distances show small, but distinct, variations as the other ligands are varied, the extremes being VII and VIII. In the former there is a multiple bond between Mo and NNH<sub>2</sub> of only 1.762 (12) Å while in the latter, due to the powerful Mo-Mo bond,<sup>37</sup> the Mo-N(pyridine) bond is 2.548 (8) Å long. In the other compounds, the variations are surprisingly small. For instance, in the molybdenyl dimer IX the formal valence state of Mo is +5 while in III it is clearly 0; nonetheless the Mo-N distances are virtually identical.

Internal comparisons of our molecular parameters show that the imine nitrogen forms a shorter Mo-N bond (Mo-N1 = 2.182 (10) Å) than the pyridine nitrogen (Mo-N2 = 2.258 (11) Å) the difference being relevant at the 5 $\sigma$  level. However, this has no effect on the trans carbonyl carbons, both of whose Mo-C distances are identical within less than 1 $\sigma$ . The same comment can be made of the CO bonds.

**Stereochemical Aspects.** In what follows, we shall refer to plane b of Table IV as the *ligand plane*. This plane contains, with very minor deviations, all the atoms of the pyridine ring plus C16, H16, N1, and the Mo atom. Besides the Cp ring which can rotate around the Mo-ring centroid vector and the methyl group which can rotate around the C8-C9 vector, there are two major sources for different conformations within the cation A: first, the conformers that arise from rotation of the entire chiral fragment around the C8-N1 bond; second, the conformers that arise from changes of the torsional angle of the phenyl plane around the C8-C10 vector. This last quantity is most conveniently viewed (see Figure 1) by defining it as the torsional angle that the C10-C12 (or C11) vector makes with respect to the C8-C9 vector, around the C8-C10 bond. With respect to these rotational conformations, we can now ask whether or not, given the fact that the chiral C8 is ste-

reochemically rigid, the conformation and configuration found in the crystal is the best possible. In other words, is it a solid-state effect dictated by *intermolecular* packing forces overwhelming *intramolecular* steric needs (and not likely to be preferred in solution, for instance) or is this a sensible choice for both, solid and solution? From steric considerations,<sup>40-42</sup> the phenyl ring is the largest substituent at C8, -CH<sub>3</sub> is middle in size, and H8 is the smallest and, as such, gives rise to different degrees of crowding with adjacent groups as the chiral carbon attempts to rotate about the C8-N1 bond (in the S configuration). Below, we describe (a) the angular arrangement that the vectors between C8 and its substituents make with respect to the ligand plane and (b) the closest contacts between the substituents at C8 and adjacent *intramolecular* fragments. Later we shall describe how rotation about C8-N1, of the entire S-chiral entity, affects the intramolecular contacts and answer the question posed above.

**Conformation in the Crystal.** The crystal structure determination shows that the big substituent, the phenyl ring, projects out of the complex, opposite the cyclopentadienyl ring, like a flagpole. The bond from C8 to the phenyl ring carbon (C10) makes an angle of 90.76° with the ligand plane (see Figure 1). The torsional angle of the phenyl ring (defined above) is -62.55°, using the IUPAC notation.<sup>43</sup>

The vector C8-C9, from the asymmetric carbon to the methyl group, forms a torsional angle of -36.21° with respect to the vector C16-N1, the latter being exactly in the ligand plane. Note that by virtue of C8 being tetrahedral the methyl carbon is directed out of the ligand plane, away from the metal, and toward the hydrogen H16. The contacts between the phenyl hydrogens and H8 are normal packing contacts,<sup>44</sup> the shortest being 2.196 Å (H12-H8), and the shortest contact between phenyl hydrogens and H16 is 2.46 Å (larger than packing contacts<sup>44</sup>). Contacts between Cp hydrogens with all other atoms exceed 2.50 Å, as is the case between H8 and all other atoms, except for that mentioned above. That leaves the methyl (C9) hydrogens to consider. Here we find that H9(2) and H9(3) are nicely oriented to avoid bad contacts but that H9(1) makes a contact with H16 of only 1.997 Å. This is one of the closest H...H contacts recorded and falls in the range of those interannular contacts found in *trans*-1,6-cyclodecanediol by Ermer, Dunitz, and Bernal.<sup>45</sup> While the C-C-C and C-C-H angles reported here are *normal* in

the sense defined by the neutron diffraction results of Ermer, Dunitz, and Bernal,<sup>45</sup> the C16–H16 distance of 0.95 (1) Å is a little shorter than the true value of 1.05 Å for a normal C–H distance (the methyl carbon positions are calculated and, therefore, of the right length). Consequently, if any error has been introduced in calculating the H9(1)–H16 contact, we have foreshortened it. Thus, we conclude that this is the only short intramolecular contact for this conformation and configuration, but it is a bad one. As mentioned earlier the steric interaction H9(1)–H16 may be responsible for the bending of C8 out of the ligand plane and for the relatively large angle N1–C8–C9 of 113.72°, both of which help to minimize the steric interaction H9(1)–H16.

**Other Conformations the Molecule Can Acquire.** In principle, the molecule could prefer other conformations in fluid media by rotation around N1–C8 while retaining *S* chirality at C8. The simplest ones are those generated by rotation of the phenyl ring about the C8–C10 vector. While in the present conformation the closest contacts between the phenyl ring hydrogens H11 and H12 with H8, H9(1,2,3), and H16 are larger than 2.4 Å, rotation about the C8–C10 vector produces, under the most unfavorable situations, contacts as short as 1.1–1.2 Å, which would be totally unacceptable. The question now is this: can all unacceptable contacts be relieved by rotation of the entire chiral group about the N1–C8 vector? The answer is best described in steps. (1) Counterclockwise rotation by about 35° would bring C9 into the ligand plane making H9(1,2,3)–H16 contacts now as short as 1.8 Å whereas the distance between phenyl ring hydrogens and the C2–O2 carbonyl atoms would be about 2.8 Å, in the most favorable orientation. However, phenyl contacts were not a problem before, so that rotation by –35° would make the situation worse than before at methyl C9. (2) Rotation by –70° leads to the same steric problems as in the conformation found in the crystal, the difference being that the methyl group is now on the opposite side of the ligand plane. However, the phenyl ring begins to get into steric problems with the C2–O2 group. (3) On further rotation in the same direction, the ortho hydrogens and ortho carbons of the phenyl ring would come into unacceptably short contacts with C2–O2 and with the hydrogens of C<sub>5</sub>H<sub>5</sub>. In the least sterically crowded situations, the closest contacts between Cp hydrogens and the phenyl ring would be as short as 1.6–1.7 Å. At the same time, the ortho hydrogens of the phenyl ring would make contacts with H9(1,2,3) of 1.8–1.9 Å. (4) After a rotation of about –240°, the phenyl ring can find a position intermediate between H16 and H9(1,2,3) which relieves packing problems but, at this point, the methyl group hydrogens would make contacts ranging from 1.7 to 1.8 Å with the C<sub>5</sub>H<sub>5</sub> hydrogens. Finally, further rotation produces short contacts between the phenyl ring ortho hydrogens and H16 and H9(1,2,3), respectively, which are not relieved until we get back to the point of departure. Consequently, in spite of the bad H16–H9(1) contact of 1.997 Å, the conformation found in the crystal seems, by far, to be the most favorable conformation if the chiral carbon is *S*. Further, it is the conformation which allows the bulky phenyl ring the widest limits of rotation.

As mentioned in the Introduction there is an equilibrium between the two diastereoisomers A and B differing only in the configuration at the Mo atom. Isomer A, the structure of which has been discussed, is present in the equilibrium mixture to the extent of only 40% compared to 60% of isomer B.<sup>15</sup> It would be interesting to know what the conformation of the asymmetric center C8, and the arrangement of its substituents, would be in the other diastereoisomer with respect to the ligand plane and to the rest of the molecule. Therefore, a structure determination of isomer B, favored in the equilibrium, is in progress.

**Specification of Configuration at the Metal Atom.** Using the extension of the *R,S* system<sup>46</sup> to *polyhapto* ligands in organometallic complexes<sup>47</sup> the priority sequence of the ligands in compounds A and B is C<sub>5</sub>H<sub>5</sub> > N(imine) > N(pyridine) > CO. To define the ranking of the two nitrogen atoms in the priority sequence, the rules for unsaturated and aromatic compounds<sup>46</sup> of Cahn, Ingold, and Prelog were used. Then, according to the sequence rule of the *R,S* system the configuration at the Mo atom in isomer A is *S*. The configurational assignment remains the same when the molecule is treated as octahedral with a phantom ligand at the sixth coordination position<sup>46</sup> or as tetrahedral with the two *cis* carbonyl ligands representing a stereochemical unit and entering the priority sequence as two times the atomic number of carbon.

The molecule under consideration, like all square-pyramidal compounds C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>LL\* with L and L\* as well as the two CO ligands *cis* to each other, belongs to chirality class "a" according to Ruch<sup>48–50</sup> since exchange of the two nitrogen coordination centers inverts the configuration at the metal atom. Also the transition state of the intramolecular inversion at the metal center, obtained by rotating NN\* by 90° with respect to the metal atom, contains a symmetry plane which passes through the midpoint of the C<sub>5</sub>H<sub>5</sub> ring, the Mo atom, and the two N atoms and which bisects the angle between the two carbonyls.<sup>12–14</sup> We are aware of the fact that the assignment of configuration will become ambiguous and arbitrary when the carbonyl groups are in position 3 or even 2 and 3 of the priority sequence.

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**Registry No.** Isomer A, 40854-36-2.

**Supplementary Material Available:** A listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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