Absolute Configurations of Organometallic Compounds. Part 6.† The Crystal Structure and Absolute Configuration of $(-)_{578}$-Carbonyl(η-cyclopentadienyl){[(*S*)-methyl(1-phenylethyl)amino]diphenylphosphine}-nitrosylmolybdenum

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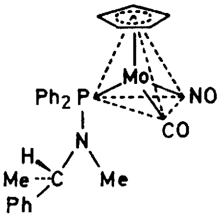
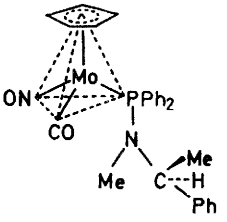
A structural analysis of the title compound has been carried out giving a final *R* of 0.043. Comparison of the observed and calculated parameters of the Bijvoet pairs has allowed the absolute configuration to be determined as *R* at the Mo atom and *S* at the asymmetric carbon atom. The substance crystallizes in space group $P2_12_12_1$ with unit-cell constants of $a = 12.612(1)$, $b = 13.856(2)$, $c = 14.174(2)$ Å, and $Z = 4$. There is no crystallographic disorder between the CO and NO groups [Mo–C(O) and Mo–N(O) 1.940(14) and 1.809(10) Å]. The compound shows the first example of chirality at a metal centre being determined by the difference between the similar ligands CO and NO, and the first example of the class of compounds [Mo(η-C_5H_5)$L^1L^2L^3$] (' three-legged ' piano stools) whose structure has been determined, the bond lengths being similar, but not the same, as those of the class [Mo(η-C_5H_5)$L^1L^2L^3L^4$] (' four-legged piano stools).

THE optically active amino-phosphine $(+)_{578}$-PPh_2-[NMe(CHMePh)], hereafter referred to as PPh_2R^* and prepared starting from (*S*)$(-)_{578}$-N[CH(Me)Ph]H_2 [3] has been used for the synthesis of a variety of optically active organometallic compounds of Mn,[3,4] Fe,[5,6] and Mo.[7,8]

In the reaction of [Mo(η-C_5H_5)$(CO)_2$(NO)] with PPh_2R^* one of the two enantiotopic CO groups is replaced by PPh_2R^*, and a pair of diastereoisomers (−)- and (+)-[Mo(η-C_5H_5)(CO)(NO)(PPh_2R^*)], (1a) and (1b), is formed.[7,8] Isomers (1a) and (1b), which are configurationally stable in solution as well as in the solid state, can be separated and obtained optically pure by preparative liquid chromatography or fractional crystallization.[7,8] An interesting feature of the pair is the similarity of the two ligands, carbonyl and nitrosyl, at the asymmetric Mo atom. Despite the fact that both, CO and NO, are linear two-atom ligands, diastereoisomers (1a) and (1b) differ markedly in their ^1H n.m.r. spectra, optical rotation, solubility, and chromatographic behaviour.[7,8]



(1a)



(1b)

The absolute configuration of all the PPh_2R^* derivatives is unknown and the assignments of relative configurations have only been made on the basis of chemical and chiroptical correlations.[9,10] Therefore it seemed desirable to isolate one of the compounds in crystalline form and to determine its absolute configuration by means of *X*-ray diffraction. Here we present the results of a structural analysis of $(-)_{578}$[Mo(η-C_5H_5)(CO)(NO)(PPh_2R^*)] (1a).

EXPERIMENTAL

The compound was characterized by the following physical properties available prior to the *X*-ray study: (*i*) crystals were obtained from methylene chloride–methanol (1 : 3) solution; [7,8] (*ii*) the optical rotations of benzene solutions of the bulk material were α (25 °C, 546 nm) = −570° and α (25 °C, 365 nm) = 2 450°.[7,8] A red-orange crystal was selected on the basis of the fact that it was transparent and, despite being a fragment, was reasonably uniform in size in all directions. The minimum and maximum dimensions were *ca.* 0.30 and 0.40 mm. Such characteristics were desirable in order to avoid absorption effects influencing the differences in intensities of Friedel pairs needed in determining absolute configurations.

Preliminary cell parameters were determined with a precession camera equipped with a Polaroid cassette, and the systematic absences obtained from isolated layers indicated the space group $P2_12_12_1$. The crystal was then transferred to a computer-controlled Enraf–Nonius CAD-4 diffractometer equipped with a high-density graphite monochromator using Mo-K_α radiation. The crystal was centred automatically using the sub-routines SEARCH, INDEX, and DETCELL [11] and then four sets of 15 reflections (maximum number for which the instrument can be programmed each time) were centred automatically in order

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† Part 5 is ref. 1, part 4 as ref. 2. This paper is also part 52 of the series ' Optically Active Transition-metal Compounds;' part 51 is ref. 3.

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[11] Instruction Manual, CAD-4-System, Enraf-Nonius, Delft, 1972.

to determine accurately the cell constants. These 60 reflections were chosen because of their intensity and all fell in the range of $20 \leqslant 2\theta \leqslant 36°$. The final determination of the cell parameters was carried out by a least-squares fit of the 2θ values of those 60 reflections using the program PARAM of the '*X*-RAY '72' System.[12] The computer of the diffractometer was reprogrammed to centre, once more, 15 strong reflections from the previous set of 60, making sure they were evenly distributed over the range of angular settings of the instrument (*i.e.* reflections of the type hkl, hkl, $\bar{h}kl$, $h\bar{k}l$, *etc.*, were used). The orientation matrix thus obtained was used during the course of intensity data collection.

Crystal Data.—$C_{27}H_{27}MoN_2O_2P$, $M = 539.24$, $a = 12.612(1)$, $b = 13.856(2)$, $c = 14.174(2)$ Å, $\alpha = 89.98(1)$, $\beta = 89.95(1)$, $\gamma = 89.99(1)°$, $U = 2\,476.9$ Å^3, $D_m = 1.42(1)$, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 1\,296$, space group $P2_12_12_1$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 4.25$ cm^{-1}.

The intensity set of data was collected using Mo-K_α radiation and the take-off angle of the graphite monochromator was set at 5.85°. Intensities were measured using the θ—2θ technique and the scan rate used during data collection was variable and determined by a fast prescan (5° min^{-1}) which was then used to determine the value necessary to accumulate 2 000 counts above background, minimum. The fastest rate allowed was *ca.* 7° min^{-1} and the maximum time allowed for a reflection to accumulate 2 000 counts was 450 s. If the time necessary to accumulate 2 000 exceeded 450 s the reflection was deemed absent and not scanned. Previous experience with our instrument, using similar substances, indicated that most of the reflections unable to meet this criterion would be too weak to be reliable and, generally, had intensities below 2 or $3\sigma(I)$. If a given reflection was measured during the pre-scan to exceed 50 000 counts s^{-1} an attenuator was used and the computer indicated this fact by a suitable code index entered into the magnetic tape record. Backgrounds were collected for 25% of the total scan time at each end of the scanning range, and for any intensity measured the width of the scan range was determined by means of the equation scan range $= A + B \tan\theta$ where $A = 1.00°$ and $B = 0.40°$. The settings for the horizontally variable aperture[11] were determined in the same fashion and A and B were set at 5.20 and 2.11 mm, respectively. The crystal-to-source and crystal-to-detector distances were fixed at 216 and 173 mm, respectively.

The reliability of the electronics and the stability of the crystal were checked by means of three reflections (501, $30\bar{6}$, and 092) which were measured every 48 data points. The instrument was programmed to stop data collection if any of the three reflections gave an intensity $<90\%$ of the first recorded value. Each of the three standard reflections was collected at a scanning rate that insured its integrated intensity to be close to 40 000 net counts. The instrument never stopped and an eventual analysis of the standards showed individual deviations in their intensities to remain within the range of $\pm 3\%$ of the first recorded value, for each of the three. The data crystal was saved for a determination of the intensities of Friedel pairs (see below). A total of 4 037 reflections was collected in the interval $2 \leqslant 2\theta \leqslant 60°$ of which 2 794 were found to have intensities greater than $3\sigma(I)$. These were corrected for Lorentz and polarization effects which included the effect of the partial polarization of the incident beam caused by the monochromatizing crystal. No absorption correction was made since the crystal was a fragment, but a check of two reflections measured every 5° around the scattering vector, over a range of 180°, showed this effect to be very small. A well formed crystal having[13] similar dimensions and absorption coefficient was shown to have transmission coefficients of 0.877—0.884. Thus, no serious problems were expected for either the refinement of the data nor the measurement of the intensities of Friedel pairs, as was eventually found to be the case. All the calculations were carried out with the routines of the '*X*-RAY '72' Program.[12]

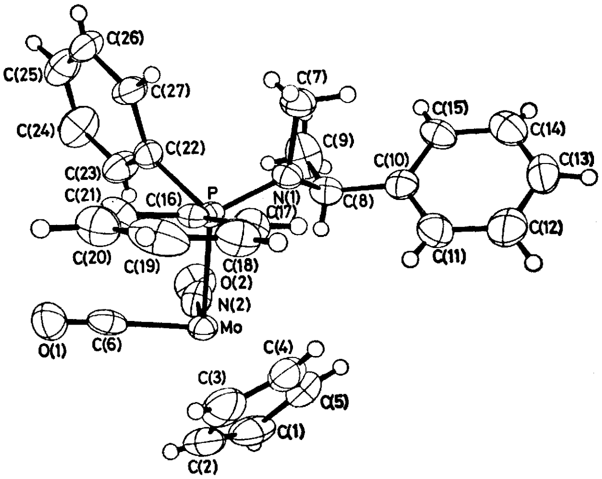

FIGURE 1 A perspective view of (1a) in its correct absolute configuration showing the numbering system used. The ellipsoids of thermal motion for the non-hydrogen atoms are 50% probability contours. Those for the hydrogen atoms are uniform isotropic envelopes of sizes suitable for display purposes. Each hydrogen bears the same number as the carbon to which it is attached except for the two methyl carbons C(7) and C(9). As shown in Table 2, C(7) has H(28), H(29), and H(30) attached to it while C(9) is associated with H(31), H(32), and H(33)

Solution and Refinement of the Structure.—Density measurements indicated that there are four molecules in the unit cell with space group $P2_12_12_1$. Therefore, the asymmetric unit should have one Mo and one P atom which we readily found in a Patterson function. These atoms were used to phase a structure-factor calculation which was followed by a refinement of the scale factor. All the other atoms were easily found from Fourier syntheses and a refinement of the structure with all the atoms vibrating isotropically gave a discrepancy factor R of 0.093. Conversion of the thermal parameters into anisotropic motion reduced R to 0.059 and introduction of the hydrogen atoms at their theoretically calculated positions (with $B = 4.04$ Å^2 and a C–H distance of 0.95 Å) lowered R to 0.055. At this point the hydrogen positions were recalculated and refinement of the heavy atoms with anisotropic motion and of the hydrogen atoms with isotropic motion led to convergence with $R = 0.043$ and with $R' = [\Sigma w(F_o - kF_c)^2/\Sigma(wF_o)^2]^{\frac{1}{2}} = 0.053$. The weighting scheme used was that described in ref. 12 as $w = \sigma(|F_o|)^{-2}$.

Throughout the refinement the atomic scattering curves of

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[12] 'The *X*-RAY System of Crystallographic Programs,' eds. J. M. Stewart, G. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Technical Report No. 192, Computer Science Center, University of Maryland, 1972.

[13] E. F. Epstein, A. Clearfield, and I. Bernal, *J. Coordination Chem.*, 1977, **6**, 227.

Cromer and Mann[14] were used for the heavy atoms together with the hydrogen scattering curve of Stewart *et al.*[15]

TABLE 1

Positional parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.215 67(9)	−0.179 14(8)	0.134 11(7)
P	0.237 5(2)	−0.194 8(2)	0.304 2(2)
N(1)	0.360 7(1)	−0.175 9(7)	0.348 0(6)
N(2)	0.207 8(9)	−0.048 8(7)	0.134 5(8)
C(1)	0.287 0(2)	−0.210 9(14)	−0.016 4(10)
C(2)	0.209 6(16)	−0.276 4(13)	0.000 2(11)
C(3)	0.241 0(14)	−0.336 8(11)	0.075 5(12)
C(4)	0.339 9(12)	−0.304 7(12)	0.104 9(10)
C(5)	0.371 4(13)	−0.227 6(13)	0.049 3(11)
C(6)	0.064 9(11)	−0.195 5(9)	0.155 8(8)
C(7)	0.379 7(10)	−0.187 0(11)	0.450 3(8)
C(8)	0.428 4(10)	−0.101 1(9)	0.304 3(9)
C(9)	0.403 3(13)	0.000 3(11)	0.335 3(14)
C(10)	0.546 6(11)	−0.130 6(9)	0.314 7(9)
C(11)	0.584 8(12)	−0.209 0(11)	0.266 8(10)
C(12)	0.689 5(13)	−0.237 4(13)	0.273 8(11)
C(13)	0.755 9(10)	−0.187 7(13)	0.332 5(9)
C(14)	0.721 1(13)	−0.111 1(11)	0.382 7(9)
C(15)	0.614 8(10)	−0.082 8(9)	0.373 8(10)
C(16)	0.210 2(9)	−0.321 3(8)	0.337 3(6)
C(17)	0.292 0(11)	−0.387 8(8)	0.338 2(8)
C(18)	0.268 4(12)	−0.485 8(9)	0.351 5(9)
C(19)	0.165 5(14)	−0.515 0(10)	0.365 4(11)
C(20)	0.084 3(12)	−0.450 3(9)	0.365 4(11)
C(21)	0.106 4(10)	−0.351 2(9)	0.352 0(9)
C(22)	0.144 6(9)	−0.126 0(8)	0.377 4(9)
C(23)	0.094 5(12)	−0.045 1(10)	0.343 7(9)
C(24)	0.026 4(14)	0.010 4(11)	0.396 1(12)
C(25)	0.010 2(13)	−0.014 2(12)	0.489 9(12)
C(26)	0.057 4(12)	−0.094 0(12)	0.528 2(9)
C(27)	0.124 3(11)	−0.152 4(10)	0.473 4(8)
O(1)	−0.024 0(8)	−0.214 1(7)	0.168 4(1)
O(2)	0.206 8(10)	0.037 3(6)	0.131 9(8)
H(1)	0.290(16)	−0.188(13)	−0.047(11)
H(2)	0.156(11)	−0.276(9)	−0.012(10)
H(3)	0.199(10)	−0.377(9)	0.090(8)
H(4)	0.382(11)	−0.324(11)	0.146(11)
H(5)	0.434(15)	−0.200(14)	0.069(13)
H(8)	0.417(12)	−0.115(11)	0.252(10)
H(11)	0.540(9)	−0.239(7)	0.237(8)
H(12)	0.715(9)	−0.291(8)	0.238(7)
H(13)	0.823(9)	−0.199(8)	0.327(8)
H(14)	0.759(12)	−0.090(10)	0.402(10)
H(15)	0.594(11)	−0.044(10)	0.407(10)
H(17)	0.358(10)	−0.378(8)	0.331(8)
H(18)	0.319(11)	−0.514(10)	0.351(11)
H(19)	0.151(10)	−0.567(9)	0.381(9)
H(20)	0.010(8)	−0.466(7)	0.370(8)
H(21)	0.053(10)	−0.321(10)	0.339(9)
H(23)	0.104(12)	−0.035(11)	0.298(11)
H(24)	−0.002(14)	0.046(13)	0.387(13)
H(25)	−0.038(11)	0.022(10)	0.523(10)
H(26)	0.051(14)	−0.103(13)	0.575(13)
H(27)	0.161(9)	−0.206(9)	0.502(9)
H(28)	0.455(11)	−0.189(11)	0.458(9)
H(29)	0.364(10)	−0.239(8)	0.472(8)
H(30)	0.343(10)	−0.147(9)	0.476(9)
H(31)	0.408(10)	0.004(9)	0.398(9)
H(32)	0.441(12)	0.037(10)	0.308(10)
H(33)	0.342(15)	0.002(13)	0.327(13)

Correction of these curves for anomalous dispersion in the cases of Mo and P was made using the values in the International Tables.[16] Table 1 lists the atomic positional parameters. Bond lengths and angles are listed in Tables 2 and 3, respectively, and equations of least-squares planes through important groups of atoms are given in Table 4 together with the distances of relevant atoms from such planes. The drawings (Figures 1—3) were obtained with ORTEP 2[17] as locally implemented at the Houston computer centre. However, the line of sight was automatically chosen as that along which there is minimum overlap by a

TABLE 2

Bond distances (Å)

Mo–P	2.436(3)	C(19)–C(20)	1.362(21)
Mo–C(1)	2.357(17)	C(20)–C(21)	1.413(18)
Mo–C(2)	2.329(16)	C(21)–C(16)	1.388(17)
Mo–C(3)	2.359(16)		
Mo–C(4)	2.375(16)	C(22)–C(23)	1.373(19)
Mo–C(5)	2.399(17)	C(23)–C(24)	1.371(22)
Mo–C(6)	1.940(14)	C(24)–C(25)	1.388(24)
Mo–N(2)	1.809(10)	C(25)–C(26)	1.367(23)
		C(26)–C(27)	1.404(20)
P–N(1)	1.694(9)	C(27)–C(22)	1.432(17)
P–C(16)	1.847(12)		
P–C(22)	1.832(12)	C(1)–H(1)	0.54(18)
		C(2)–H(2)	0.70(14)
N(2)–O(2)	1.193(13)	C(3)–H(3)	0.80(13)
C(6)–O(1)	1.164(17)	C(4)–H(4)	0.84(15)
		C(5)–H(5)	0.92(19)
N(1)–C(8)	1.479(16)	C(8)–H(8)	0.78(15)
N(1)–C(7)	1.478(14)	C(11)–H(11)	0.82(11)
C(8)–C(9)	1.505(20)	C(12)–H(12)	0.95(13)
C(8)–C(10)	1.552(19)	C(13)–H(13)	0.87(11)
C(1)–C(2)	1.353(30)	C(14)–H(14)	0.62(14)
C(2)–C(3)	1.413(24)	C(15)–H(15)	0.75(14)
C(3)–C(4)	1.388(23)	C(17)–H(17)	0.84(13)
C(4)–C(5)	1.385(23)	C(18)–H(18)	0.74(14)
C(5)–C(1)	1.433(27)	C(19)–H(19)	0.77(12)
		C(20)–H(20)	0.96(10)
C(10)–C(11)	1.369(20)	C(21)–H(21)	0.81(13)
C(11)–C(12)	1.382(22)	C(23)–H(23)	0.67(15)
C(12)–C(13)	1.367(22)	C(24)–H(24)	0.62(18)
C(13)–C(14)	1.350(22)	C(25)–H(25)	0.91(14)
C(14)–C(15)	1.402(20)	C(26)–H(26)	0.68(18)
C(15)–C(10)	1.371(19)	C(27)–H(27)	0.96(12)
		C(7)–H(28)	0.95(14)
C(16)–C(17)	1.384(17)	C(7)–H(29)	0.81(12)
C(17)–C(18)	1.403(17)	C(7)–H(30)	0.80(13)
C(18)–C(19)	1.374(23)	C(9)–H(31)	0.89(13)
		C(9)–H(32)	0.80(15)
		C(9)–H(33)	0.78(19)

TABLE 3

Angles (°)

N(2)–Mo–C(6)	93.6(5)	C(17)–C(16)–C(21)	120.2(1.1)
N(2)–Mo–P	95.3(4)	C(16)–C(21)–C(20)	119.8(1.2)
C(6)–Mo–P	86.8(4)	C(21)–C(20)–C(19)	119.4(1.3)
Mo–P–N(1)	116.9(3)	C(20)–C(19)–C(18)	121.2(1.3)
Mo–P–C(22)	116.3(4)	C(19)–C(18)–C(17)	120.3(1.3)
Mo–P–C(16)	108.4(3)	C(18)–C(17)–C(16)	119.2(1.2)
C(22)–P–C(16)	103.3(5)		
C(16)–P–N(1)	103.0(5)	C(27)–C(22)–C(23)	117.2(1.2)
C(22)–P–N(1)	107.3(5)	C(22)–C(23)–C(24)	123.9(1.3)
P–N(1)–C(8)	119.0(7)	C(23)–C(24)–C(25)	118.2(1.4)
P–N(1)–C(7)	119.5(8)	C(24)–C(25)–C(26)	121.0(1.5)
C(7)–N(1)–C(8)	112.9(9)	C(25)–C(26)–C(27)	120.6(1.3)
N(1)–C(8)–C(9)	114.2(1.1)	C(26)–C(27)–C(22)	119.1(1.2)
N(1)–C(8)–C(10)	109.3(1.0)		
C(9)–C(8)–C(10)	114.8(1.1)	C(2)–C(1)–C(5)	108.3(1.5)
C(8)–C(10)–C(15)	122.2(1.1)	C(1)–C(2)–C(3)	109.0(1.7)
C(8)–C(10)–C(11)	120.0(1.2)	C(2)–C(3)–C(4)	106.8(1.5)
		C(3)–C(4)–C(5)	109.5(1.4)
C(11)–C(10)–C(15)	117.7(1.3)	C(4)–C(5)–C(1)	106.3(1.5)
C(10)–C(15)–C(14)	121.4(1.2)		
C(15)–C(14)–C(13)	118.9(1.3)	Mo–C(6)–O(1)	173.9(1.1)
C(14)–C(13)–C(12)	121.2(1.4)	Mo–N(2)–O(2)	176.8(1.1)
C(13)–C(12)–C(11)	119.0(1.5)		
C(12)–C(11)–C(10)	121.8(1.4)		

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[15] R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[16] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1967, vol. 3, p. 215.

[17] C. K. Johnson, 'ORTEP 2, A Fortran-Ellipsoid Plot Program for Crystal Structure Illustration,' ORNL-5138, Oak Ridge, Tennessee, 1972.

computer program kindly provided by Professor R. E. Davis, University of Texas, Austin. A table of measured and of calculated structure factors and a list of anisotropic thermal parameters are available as Supplementary Publication No. SUP 22335 (18 pp.)*

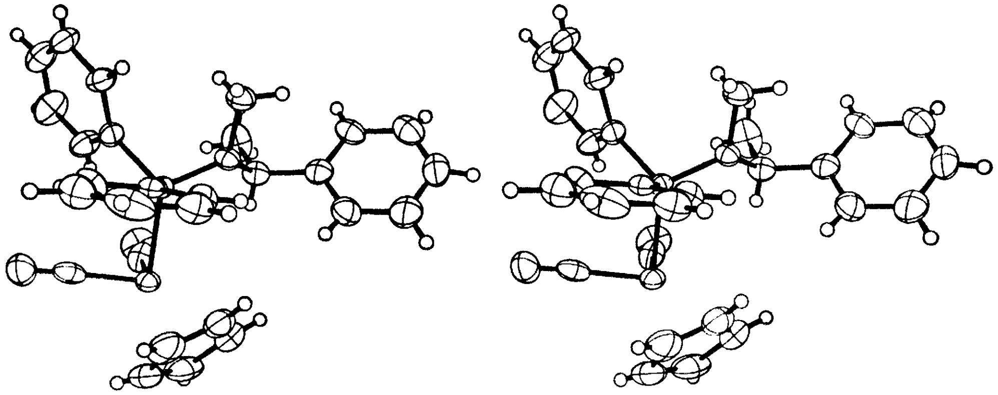

FIGURE 2 A stereodiagram of the molecule in its correct absolute configuration. The right-hand view of this stereo-pair was used for the perspective view shown in Figure 1

Determination of the Absolute Configuration.—After the structure had been completely refined a structure-factor calculation was made using the two possible configurations (xyz and $\bar{x}\bar{y}\bar{z}$) and a set of 19 reflections was chosen for which the two Friedel pairs (hkl and $\bar{h}\bar{k}l$) had a sufficiently large difference in intensity to insure there would be no error in differentiating between the two. The scanning routine [11] MODE = −1 was used and each of the 19 reflections was measured four separate times in the order (hkl, $\bar{h}\bar{k}l$, $\bar{h}\bar{k}l$, hkl, hkl, $\bar{h}\bar{k}l$, $\bar{h}\bar{k}l$, and hkl). Each scan was programmed to be run at a rate such that a minimum of 4 000 counts above background were obtained. The crystal used was that employed in the intensity-data collection and we verified that the intensities of the three standard reflections had not changed during the interval between the end of data collection and the measurement of the Friedel pairs. The set of co-ordinates accidentally chosen during the initial solution of the structure was correct, as shown in Table 5. The refinement of the complete set of data using the absolute configuration chosen on the basis of 19 Friedel pairs gave $R = 0.043$, whereas reversing the co-ordinates (to $-x$, $-y$, $-z$) for all the atoms gave $R = 0.045$. Finally the absolute configuration at the optically active carbon of the amine is predicted correctly to be *S*, a fact known to the synthetic chemists but not to the crystallographers. Inasmuch as there are four possible diastereoisomers [the Mo and C(8) sites are optically active] and a crystal was chosen from the bulk of the crystallization product on the basis of quality and size only, we decided to measure the optical rotation for the data crystal itself. The signs of rotation obtained from a solution of the crystal in benzene for the two wavelengths listed in the Experimental section were verified.[8] Thus, we are certain that we did not accidentally choose a crystal comprising a small amount of diastereoisomeric impurity present in the bulk of the major component.

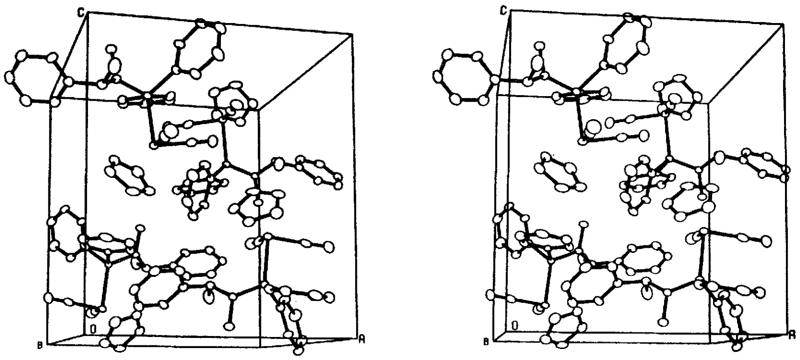

FIGURE 3 A stereodiagram showing the molecules in their correct absolute configuration and the mode of packing in the unit cell

Since it is possible to start with the (*R*)-amine and to grow crystals of similar quality to those described above, we decided to carry out the same measurements on one such crystal. It was chosen to be of about the same shape and size as the original data crystal, mounted on the diffractometer and aligned as described earlier, and we verified that it had the same space group and cell constants as the other enantiomer. Measurement of the same 19 reflections gave exactly the opposite results as those listed in Table 6, which require that the absolute configuration of the molecule be reversed from that shown in Figure 1. Again, the crystal used in the Friedel-pair test was dissolved in benzene and its optical rotation was shown to be that of the parent bulk material.

DISCUSSION

Figure 1 depicts the absolute configuration of the molecule and this view clearly shows that, if we exclude the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

η-C_5H_5 ring, the remaining fragment is part of an octahedron with the Mo atom at the origin. This qualitative observation is reinforced by the values of the angles around the central metal atom listed in Table 3 [N(2)–Mo–C(6) 93.6(5), N(2)–Mo–P 95.3(4), and C(6)–Mo–P 86.8(4)°]. Thus, [Mo(η-C_5H_5)(CO)(NO)(PPh_2R^*)] is best viewed as a derivative of [$Mo(CO)_6$] in which three *fac* positions of the octahedron are occupied by the η-C_5H_5 ring while two more CO ligands have been replaced by a phosphine and a nitrosyl, the last two changes causing only minor rearrangements of the original geometry of the parent species.

TABLE 4

Least-squares planes in orthogonal Ångstrom space; distances (Å) of atoms from the planes are given in square brackets

Plane (*a*): C(1), C(2), C(3), C(4), C(5)

$$-0.4316x + 0.6294y + 0.6463z = -3.5517$$

[C(1) 0.0001, C(2) 0.0031, C(3) −0.0053, C(4) 0.0055, C(5) −0.0035, Mo 2.0443]

Plane (*b*): C(10), C(11), C(12), C(13), C(14), C(15)

$$-0.2500x - 0.6055y + 0.7555z = 2.7538$$

[C(10) −0.0119, C(11) 0.0120, C(12) −0.0046, C(13) −0.0028, C(14) 0.0026, C(15) 0.0047]

Plane (*c*): C(16), C(17), C(18), C(19), C(20), C(21)

$$0.1088x + 0.1201y + 0.9868z = 4.4795$$

[C(16) −0.0075, C(17) 0.0063, C(18) −0.0033, C(19) 0.0016, C(20) −0.0027, C(21) 0.0057]

Plane (*d*): C(22), C(23), C(24), C(25), C(26), C(27)

$$0.7776x + 0.5614y + 0.2832z = 1.9467$$

[C(22) 0.0060, C(23) 0.0089, C(24) −0.0168, C(25) 0.0098, C(26) 0.0052, C(27) −0.0131]

Plane (*e*): P, N(2), C(6)

$$-0.5641x + 0.5865y + 0.5813z = -0.7660$$

[Mo −1.1188]

TABLE 5

Determination of the absolute configuration for the diastereoisomer of (1) having α (546 nm) = −580° and α (365 nm) = 2 450°

Reflection number	Indices	F_c		*F* ratio	
		hkl	$\bar{h}\bar{k}\bar{l}$	Calc.[a]	Obs.[b]
1	2, 3, 2	62.36	66.60	0.94	0.94
2	4, 2, 2	78.49	76.18	1.03	1.03
3	1, 2, 2	103.18	104.47	0.99	0.98
4	11, 6, 2	21.94	20.45	1.07	1.09
5	1, 5, 3	76.04	76.92	0.99	0.98
6	1, 1, 3	178.86	177.31	1.01	1.01
7	2, 5, 3	51.35	52.88	0.97	0.97
8	2, 2, 4	12.26	9.21	1.33	1.25[c]
9	2, 5, 4	55.39	56.50	0.98	0.97
10	1, 4, 4	66.12	65.60	1.01	1.00
11	1, 1, 4	51.98	54.25	0.96	0.98
12	1, 4, 7	100.79	101.55	0.99	0.99
13	1, 2, 7	108.80	110.28	0.99	0.98
14	2, 1, 7	83.10	84.45	0.98	1.00
15	3, 3, 7	34.36	35.63	0.96	0.98
16	3, 1, 9	24.54	26.73	0.92	0.93
17	2, 2, 10	24.48	26.04	0.94	0.93
18	2, 7, 5	72.14	72.94	0.99	0.99
19	2, 6, 8	30.14	31.17	0.97	0.97

[a] Calc. *F*(*hkl*)/Calc. *F*($\bar{h}\bar{k}\bar{l}$). [b] Ratio of experimentally measured *F*(*hkl*)/*F*($\bar{h}\bar{k}\bar{l}$). [c] This is the weakest reflection in the list and *F*($\bar{h}\bar{k}\bar{l}$) was measured with least precision but, clearly, its ratio to *F*(*hkl*) satisfies the test of being the smaller of the two by a wide margin.

TABLE 6

Comparison of Mo–N distances in molybdenum nitrosyls

Compound	Distance/Å		Angle/°	Distance[a]/Å	Ref.
	Mo–N	N–O	Mo–N–O	Mo–C_5H_5	
(1) [Mo(η-C_5H_5)(CO)(NO)(PPh_2R^*)]	1.809(10)	1.193(13)	176.8(11)	2.044	*b*
(2) [Mo(NO)($S_2CNBu^t{}_2$)$_3$]	1.731(8)	1.154(9)	173.2(7)		*c*
(3) [Mo(η-C_5H_5)$_2$(σ-C_5H_5)(NO)]	1.751(3)	1.207(4)	179.2(2)	2.140	*d*
				2.145	
(4) [MoMe(η-C_5H_5)$_2$(NO)] [e]	1.75(1)	1.23(1)	178(2)	2.180	*f*
	1.76(1)	1.21(1)	178(1)	2.109	
				2.132	
				2.137	
(5) [Mo(η-C_5H_5)I(NO)(NH_2NHPh)][BF_4]	1.780(4)	1.188(5)	170.6(3)	*g*	*h*
(6) [{Mo(η-C_5H_5)I(NO)}$_2$$NNMe_2$]	1.765(12)			*g*	*i*
	1.763(12)				
(7) [$MoCl_2(NO)_2(PPh_3)_2$]	1.826(7)	1.223(12)	180.0(10) [j]		*k*

[a] Distance of Mo from the C_5H_5 plane. [b] This work. [c] T. F. Brennan and I. Bernal, *Inorg. Chim. Acta*, 1973, **7**, 203. [d] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 1969, **91**, 2528. [e] Two independent molecules in the asymmetric unit. [f] F. A. Cotton and G. A. Rusholme, *J. Amer. Chem. Soc.*, 1972, **94**, 402. [g] Not given and no crystallographic co-ordinates available in the original communication. [h] N. A. Bailey, P. D. Frisch, J. A. McCleverty, N. W. J. Walker, and J. Williams, *J.C.S. Chem. Comm.*, 1975, 350. [i] W. G. Kita, J. A. McCleverty, B. E. Mann, D. Seddon, G. A. Sim, and D. I. Woodhouse, *J.C.S. Chem. Comm.*, 1974, 132. [j] Corrected values, see footnote *k*. [k] Values quoted by J. H. Enemark and R. D. Feltham, *Co-ordination Chem. Rev.*, 1974, **13**, 339 as a correction to M. O. Vissher and K. G. Kaulton, *J. Amer. Chem. Soc.*, 1972, **94**, 5923.

Differentiation between CO and NO in this molecule was arrived at by refinement and by the fact that the better refinement was that for which the choice of NO gave a Mo–N distance of 1.809(10) Å while the chosen CO resulted in a Mo–C distance of 1.940(14) Å. Table 6 shows examples of Mo–N(nitrosyl) bond lengths which demonstrate that, for a wide variety of compounds, the Mo–N distance ranges from *ca.* 1.73 to 1.83 Å. On the other hand, values of Mo–C(carbonyl) of 1.984(14) and 1.988(14), 1.973(6) and 2.020(6), 1.965(8) and 1.964(14), 1.973(3) and 1.996(3), and of 1.934(10) Å have been reported, respectively, for [Mo(η-C_5H_5)(CO)$_2$(N–N*)][PF_6] [18] [(11) in Table 7], [Mo{HB(pz)$_3$}(CO)$_2$(NNPh)] (pz = pyrazolyl),[19] [Mo(CO)$_3$(NC_5H_5)(N_2-

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[18] I. Bernal, S. J. LaPlaca, J. Korp, H. Brunner, and W. A. Herrmann, *Inorg. Chem.*, 1978, **17**, 382.

[19] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725.

$C_{10}H_8)]$,[20] $[Mo\{(NC)_2CC(CN)_2Me\}(\eta\text{-}C_5H_5)(CO)_2(PPh_3)]$ (12),[21] and $[Mo(\eta\text{-}C_5H_5)(CO)(NCO)(PPh_3)_2]$ (8).[22] Therefore, our differentiation between CO and NO is sound and it implies that we have no crystallographic disorder or any indication of a diastereoisomeric mixture at the metal centre in the crystal studied. The stereochemical rigidity at the chiral molybdenum and carbon atoms has been demonstrated spectroscopically,[7,8] and by the fact that we have independently determined the absolute configuration of both enantiomers accessible starting from (*R*)(+)- and (*S*)(−)-1-phenylethylamine during the course of this study (see above). Since CO–NO disorder is a common phenomenon in solid-state samples of organometallics,[23] it was crucial to make this point clear and to show that we are not plagued by such problems in the current study.

TABLE 7

Comparison of $Mo–C_5H_5$ [a] and Mo–P distances in organometallics of the type $[Mo(C_5H_5)_nL_m]$ (m = 3 or 4)

	Compound	Distance/Å		Ligands L_m or co-ordinating atoms	Ref.
		$Mo\text{-}C_5H_5$	Mo–P		
(1)		2.044	2.436(3)	CO, NO, PPh_2R *	*b*
(8)	$[Mo(\eta\text{-}C_5H_5)(CO)(NCO)(PPh_3)_2]$	1.996	2.497(3) 2.500(3)	CO, NCO, 2P	22
(9)	$[Mo(C_3F_7)(\eta\text{-}C_5H_5)(CO)_3]$	1.997		3 CO, C	*c*
(10)	$[Mo\{CC(CN)_2\}(\eta\text{-}C_5H_5)Cl(PMe_3O)_2]$	1.997	2.461(2) 2.470(2)	2 PMe_3O, Cl, C	*d*
(11)	$[Mo(\eta\text{-}C_5H_5)(CO)_2(N–N^*)][PF_6]$ [e]	2.005		2 CO, 2 N	18
(12)	$[Mo\{(NC)_2CC(CN)_2Me\}(\eta\text{-}C_5H_5)(CO)_2(PPh_3)]$	2.007	2.5175(8)	2 CO, P, C	21
(13)	$[Mo(CH_2CO_2H)(\eta\text{-}C_5H_5)(CO)_3]$	2.01		3 CO, C	*f*
(14)	$[Mo(\eta\text{-}C_5H_5)(CO)_2\{SCMe(NR^*)\}]$ [g]	2.012		2 CO, (S + N)	1
(15)	$[Mo(CH_2SMe)(\eta\text{-}C_5H_5)(CO)_2]$	2.015		2 CO, (S + C)	*h*
(16)	$[Mo(COMe)(\eta\text{-}C_5H_5)(CO)_2(PPh_3)_2]$	2.018	2.473	2 CO, P, C	*i*
(17)	$[Mo(\eta\text{-}C_5H_5)(CO)_2\{NHNC(CO_2Et)(CHO)\}]$	2.022		2 CO, (N + C)	*j*

[a] C_5H_5 = η-C_5H_5 ring centroid. [b] This study. [c] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1967, **6**, 1213. [d] R. M. Kirchner and J. A. Ibers, *Inorg. Chem.*, 1974, **13**, 1667. [e] N-N* = Schiff base of pyridine-2-carbaldehyde and (*S*)-$NH_2[CH(Me)Ph]$. [f] J. K. P. Ariyaratne, A. M. Bjerrum, M. H. L. Green, M. Ishaq, C. K. Prout, and M. G. Swanwick, *J. Chem. Soc.* (*A*), 1969, 1309. [g] R* = (*S*)-NMe[CH(Me)Ph]. [i] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1968, **7**, 953. [j] J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1952.

As recently demonstrated,[1] the bonding of Mo to an η-C_5H_5 ring in organometallic compounds is influenced to some extent by the nature of the other ligands present. For a wide range of compounds discussed[1] the mean value of the $Mo–C(C_5H_5)$ bond lengths ranged from 2.31 to 2.36 Å while the standard deviation from the mean was, generally, *ca.* 0.05 Å. Thus, it is not surprising to find in the current study (Table 2) that the $Mo–C(C_5H_5)$ distances range from 2.329(16) to 2.375(16) Å and that the mean and standard deviations thereof are 2.364(26) Å. The problem with evaluating such variations is that they are affected to a meaningful degree by the magnitude of the librational motion of the C_5H_5 ring about the metal–ring centroid vector and this varies from case to case.[1] Since the problem is connected with the exact definition of two-dimensional co-ordinates of the carbons with respect to the ring plane (using an origin on that plane) and not with the definition of the plane itself, we prefer to discuss our molecule in terms of the distance between the Mo atom and the plane of the C_5H_5 ring. Of those organometallic molecules for which the central Mo atoms have C_5H_5 and NO ligands, there appear to be changes in the distance of the metal from the C_5H_5 plane [see compounds (1), (3), and (4); Table 6]; however, the extent to which the magnitude of these changes is valid is uncertain given the values of the stated errors. More important, however, is the following observation: while the closely related pair (3) and (4) seems to show differences in the $Mo–C_5H_5$(plane) distance, the two crystallographically independent, but chemically identical, molecules in (4) show internal differences in these quantities which are as large as the differences between the relevant values in (3) and (4). These uncertainties are not surprising given the errors associated with older data sets. Also, in compounds (3) and (4) the possibility of steric hindrance as a factor in determining the $Mo–C_5H_5$(plane) distance is distinctly larger than in (1). While it is tempting to argue that the shorter Mo-N(NO) distances in (3) and (4) seem to indicate a higher bond order for this bond in those substances and a concomitantly longer $Mo–C_5H_5$(plane) distance, it may be that the two adjacent C_5H_5 rings in (3) and (4) sterically hinder one another, allowing the small and effective π-acceptor NO ligand to take advantage of a sterically influenced bonding situation.

If we now address ourselves to the data listed in Table 7 we note that there is only one compound known in the structural literature of the type $[Mo(\eta\text{-}C_5H_5)L^1L^2L^3]$ while there are many of the type $[Mo(\eta\text{-}C_5H_5)L^1L^2L^3L^4]$. The former may be labelled ‘ three-legged ’ piano stools while the latter have already been labelled ‘ four-legged ’ piano stools by Churchill and Chang.[21] It is notable that the overall range of $Mo–C_5H_5$(plane) distances in the compounds in Table 7 is only 0.048 Å, so that, if a uniform standard deviation of 0.008 Å is assumed for the two compounds at the extremes, the

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[20] A. Griffiths, *J. Cryst. Mol. Structure*, 1971, **1**, 75.

[21] M. R. Churchill and S. W.-Y. Chang, *Inorg. Chem.*, 1975, **14**, 98.

[22] A. T. McPhail, G. R. Knop, C. G. Robertson, and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 205.

[23] G. Evrard, R. Thomas, B. R. Davis, and I. Bernal, *Inorg. Chem.*, 1976, **15**, 52.

difference is meaningful to the extent of 4.3σ. In accordance with previous observations from our studies,[1,18] this is a meaningful, although small, difference for this quantity especially when one considers the wide range of ligands represented.

The Mo–P bond length varies significantly from 2.436(3) Å in (1) to 2.517 5(8) Å in (12). Also, it is clear from Table 7 that the four-legged species have longer Mo–P bond lengths and shorter Mo–C_5H_5(plane) distances. This is an electronic effect. In a four-legged species the geometry is nearly square pyramidal, in a three-legged species nearly trigonal pyramidal, and while the metal in both cases is above the plane of the basal ligands, the extent to which the ligands are crowded at the base must be larger for a four- than for a three-legged species. Therefore, in the latter compounds the atoms in the ' legs ' can move farther from the C_5H_5 ring than in the former. If steric effects were to predominate, the Mo–C_5H_5 distances for $[Mo(\eta\text{-}C_5H_5)L^1L^2L^3L^4]$ compounds should be longer. Inasmuch as the reverse is true, the effect has to be electronic in origin. Aside from these general comments, we feel that meaningful comparisons of distances, angles, *etc.* should be made amongst compounds of the same classes where steric and electronic effects can be compared quantitatively. Until further examples of three-legged $Mo(C_5H_5)$ compounds are available this is not possible.

Absolute Configuration and Conformation.—If the π-bonded cyclopentadienyl ring is taken as one ligand, compound (1a) has four ligands and the configuration at the metal centre can be specified according to the *R,S* system.[24] If the extension of the *R,S* system to organometallic complexes with π-bonded ligands is used [25] and the η-C_5H_5 ligand is counted as having five times the atomic number of carbon, the priority sequence of the ligands is $\eta\text{-}C_5H_5 > PPh_2R^* > NO > CO$ and the configuration at the Mo atom in (1a) follows as *R*. Our *X*-ray determination also showed that the configuration of the 1-phenylethyl group in (1a), prepared from (*S*)(−)-1-phenylethylamine, is *S*.

Since the ligands η-C_5H_5, CO, and NO are symmetrical with respect to the metal–ligand axis, the only sources for different conformations are changes in the arrangement of the phosphine ligand and its substituents compared to the rest of the molecule. The projection of the phenyl ring attached to the phosphorus atom which is opposite to the NO group is almost perpendicular to the Mo–P bond (Figure 1). The other phenyl ring is so inclined that the *o*-hydrogen H(23) is pointing to the NO ligand: *o*-H–N and *o*-H–O distances are, respectively, 2.67 and 2.87 Å. In the crystal the P–N bond is *trans* to the CO ligand. The methyl substituent at the N atom is directed to the side opposite the Mo atom and the cyclopentadienyl ring. Figure 1 shows that the 1-phenylethyl group bound to the N atom is bent back to avoid short contacts with the *o*-hydrogen H(17) of the phenyl ring C(16)—C(21). At the asymmetric carbon atom C(8), the big phenyl substituent C(10)—C(15) projects out of the complex so that there is no steric interference with any other intramolecular neighbour. The medium size methyl group is directed to the canted phenyl ring C(22)—C(27). The small substituent H(8) at the asymmetric centre C(8) points to the interior of the complex. This specific arrangement of the N–C(8) bond and specific conformation of the (*S*)-1-phenylethyl group avoids short intramolecular contacts within the molecule.

The amino group NMe[CHMePh] in the proximity of the phosphorus atom has steric requirements similar to a phenyl ring. Also, the angle Mo–P–C(22) to the tilted phenyl ring is almost identical to the angle Mo–P–N(1) to the amine substituent (Table 3). This means that the cone angle of PPh_2R^*, according to the definition of Tolman and his co-workers,[26-28] is similar to that of PPh_3. This is corroborated by the fact that dissociation of PPh_3 and PPh_2R^* in the manganese complexes $[Mn(\eta\text{-}C_5H_5)(CO)(NO)L]$ occurs at almost the same rate.[4]

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[25] K. Stanley and M. C. Baird, *J. Amer. Chem. Soc.*, 1975, **97**, 6599.

[26] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2953.

[27] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[28] C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Amer. Chem. Soc.*, 1974, **96**, 53.