The Crystal and Molecular Structure of (η^5-C_5H_5)$(OC)_2MoC(C_6H_5)_2N(CH_3)C(C_6H_5)N(CH_3)$

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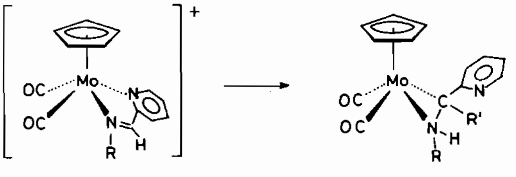
The X-ray structure of (η^5-C_5H_5)$(CO)_2MoC(C_6H_5)_2N(CH_3)C(C_6H_5)N(CH_3)$ has been determined from single crystal diffraction data. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions a = *11.803(5),* b = *12.114(6),* c = *17.198(6) Å and β = 96.61(3)°. The structure was solved by the Patterson method and refined to a final R factor of 5.1% using 2979 independent data. The molecules consist of a central Mo atom surrounded by an approximately square-pyramidal array of five ligands: the Cp ring, two carbonyls and a bidentate ligand, the latter consisting of a nitrogen and a carbon as binding atoms and forming a five membered chelate ring. The Mo atom is 2.02 and 0.99 Å from the Cp and basal square pyramidal planes, respectively. The dihedral angle between those two planes is 5.1°. The geometry of the (η^5-C_5H_5)$(CO)_2Mo$ fragment is normal. The two Mo–C(CO) and the two CO distances are slighlty different due to the* trans *effect. The distances beween the Mo atom and the binding carbon and nitrogen are 2.353(8) and 2.160(7) Å, respectively. One of the phenyl rings attached α to the Mo is close to facing the edge of the Cp ring and is held rigidly since steric hindrance could not allow large vibration about the Ph–C single bond.*

Introduction

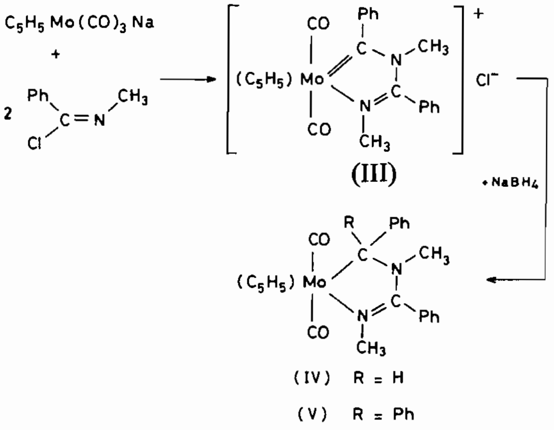
Sometime ago we reported [1] the synthesis and structure of a (h^5-C_5H_5)$Mo(CO)_2$ derivative which contained the three member ring system shown in Scheme I as compound (I)



(I) R = $-CH(CH_3)(C_6H_5)$ R' = $-CH_3$

(II) R = $-CH(CH_3)_2$ R' = $-C_6H_5$

In an effort to devise new methods for the synthesis of this type of ring system, Wachter [2] attempted to use the acyliminohalides reagents which had successfully been employed previously by Adams *et al.* [3] and by Lappert *et al.* [4] to prepare organometallics of W, Fe and Co [3] and of Rh [4]. The planned synthesis, however, resulted in the products shown in Scheme II:



(III)

(IV) R = H

(V) R = Ph

Unfortunately, the ^{1}H-nmr spectrum of compound (III, Scheme II) is quite complicated if for no other reason than that it consists of two quite similar isomers which cannot be separated by fractional crystallizations. Finally, the Cl^- or the PF_6^- salts can be reduced with $NaBH_4$ to give two neutral isomers which are readily separable and which show very similar IR spectra but *very different* ^{1}H-nmr spectra. These isomers can be separated by column chromatography and after recrystallization, one can get a pure crystalline material showing elemental analysis and mass spectral behavior compatible with (IV). A derivative of (IV), namely that with two phenyl groups at the ligand carbon (Compound V), can be obtained in crystalline form suitable for crystallographic purposes and it is the structure of that compound which is reported here. This substance can be obtained by

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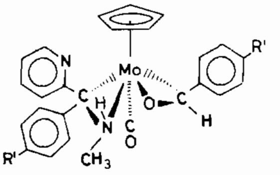
TABLE I. Summary of Data Collection and Processing Parameters.

Space Group	$P2_1/c$
Cell Constants	a = 11.803(5)Å
	b = 12.114(6)
	c = 17.198(6)
	β = 96.61(3)°
	V = 2431.2 Å^3
Molecular Formula	$MoN_2O_2C_{29}H_{26}$
Molecular Weight	530.17
Molecules per Cell	Z = 4
Density	1.45 g cm^{-3}
Absorption Coefficient	4.95 cm^{-1}
Radiation (MoKα)	λ = 0.71073 Å
Collection Range	$4° \leqslant 2\theta \leqslant 50°$
Scan Width	$\Delta\theta = (0.95 + 0.30\tan\theta)$
Maximum Scan Time	180 sec.
Scan Speed Range	0.48 to 6.70° min^{-1}
Total Data Collected	4439
Independent Data with $I > 3\sigma(I)$	2979
Total Variables	154
R $\Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	5.1
R $[\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2]^{1/2}$	4.8
Weights	$w = \sigma(F)^{-2}$
Goodness-of-fit	4.49

reacting LiPh with cation (III) instead of using $NaBH_4$.

While the crystallographic results clearly establish the nature of the diphenyl derivative of (IV), the possibility of obtaining products containing two three membered rings was not totally out of the question since we have, indeed, already reported a case of a CpMo(CO) derivative containing two such three membered rings [5], in the form of compound (VI).



(VIa) R' = H ; (VIb) R' = Me

Experimental

The details of the synthesis and the physical properties of the compound will be reported elsewhere [6]. Intensity measurements were carried out with an ENRAF-NONIUS CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing are given in Table I. Accurate

TABLE II. Atomic Coordinates and Thermal Parameters (×1000; Mo × 10000).

Atom	x/a	y/b	z/c	U11	U22	U33	U12	U13	U23
Mo	0.90303(4)	0.83332(4)	0.37937(3)	264(2)	326(3)	431(3)	–25(3)	69(2)	–45(3)
N1	0.8523(4)	0.6631(4)	0.3889(3)	33(3)	31(3)	49(3)	4(3)	–2(2)	–1(3)
N2	0.6946(4)	0.6991(4)	0.2993(3)	29(3)	27(3)	38(3)	–1(2)	–1(2)	–1(2)
O1	0.9432(4)	0.8236(5)	0.5620(3)	100(4)	72(4)	42(3)	–7(3)	–4(3)	2(3)
O2	0.7989(4)	1.0478(4)	0.4400(3)	41(3)	18(3)	49(4)	8(2)	7(3)	–19(3)
C6	0.9271(5)	0.8259(6)	0.4934(4)	44(4)	37(4)	64(5)	–6(4)	8(4)	–3(4)
C7	0.8345(5)	0.9723(6)	0.4156(4)	32(4)	55(5)	51(5)	–17(3)	–3(3)	14(4)
C8	0.7116(4)	0.8196(5)	0.3178(3)	29(3)	25(3)	36(4)	1(3)	6(3)	0(3)
C9	0.7596(5)	0.6271(5)	0.3469(3)	28(3)	32(4)	39(4)	1(3)	12(3)	0(3)
C10	0.5864(5)	0.6637(5)	0.2521(3)	36(3)	40(4)	51(4)	–6(3)	–6(3)	–2(4)
C11	0.9247(5)	0.5858(5)	0.4420(4)	50(4)	43(4)	77(6)	7(4)	–19(4)	11(4)
C1	0.9812(4)	0.8103(4)	0.2603(2)	55(2)					
C2	0.9867(4)	0.9227(4)	0.2840(2)	64(2)					
C3	1.0622(4)	0.9303(4)	0.3563(2)	66(2)					
C4	1.1034(4)	0.8225(4)	0.3773(2)	67(2)					
C5	1.0533(4)	0.7484(4)	0.3179(2)	65(2)					
C12	0.7052(3)	0.8880(2)	0.2423(2)	31(1)					
C13	0.6881(3)	1.0017(2)	0.2463(2)	39(2)					
C14	0.6908(3)	1.0672(2)	0.1799(2)	45(2)					
C15	0.7104(3)	1.0190(2)	0.1094(2)	54(2)					
C16	0.7274(3)	0.9053(2)	0.1054(2)	53(2)					
C17	0.7248(3)	0.8398(2)	0.1719(2)	42(2)					

(continued on facing page)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c	U11	U22	U33	U12	U13	U23
C18	0.6150(3)	0.8466(3)	0.3667(2)	30(1)					
C19	0.6315(3)	0.8216(3)	0.4468(2)	37(1)					
C20	0.5420(3)	0.8356(3)	0.4905(2)	48(2)					
C21	0.4360(3)	0.8746(3)	0.4541(2)	52(2)					
C22	0.4195(3)	0.8995(3)	0.3740(2)	51(2)					
C23	0.5090(3)	0.8855(3)	0.3303(2)	39(2)					
C24	0.7194(3)	0.5121(3)	0.3506(2)	33(1)					
C25	0.7777(3)	0.4251(3)	0.3211(2)	47(2)					
C26	0.7464(3)	0.3163(3)	0.3338(2)	58(2)					
C27	0.6569(3)	0.2945(3)	0.3761(2)	52(2)					
C28	0.5986(3)	0.3815(3)	0.4056(2)	49(2)					
C29	0.6298(3)	0.4903(3)	0.3929(2)	41(2)					
H1	0.9371(4)	0.7816(4)	0.2140(2)	204(14)					
H2	0.9469(4)	0.9824(4)	0.2564(2)	204(14)					
H3	1.0817(3)	0.9959(4)	0.3855(2)	204(14)					
H4	1.1553(4)	0.8034(4)	0.4230(2)	204(14)					
H5	1.0659(4)	0.6710(4)	0.3169(2)	204(14)					
H101	0.5525(5)	0.7244(5)	0.2223(3)	71(13)					
H102	0.5357(5)	0.6379(5)	0.2861(3)	71(13)					
H103	0.6011(5)	0.6060(5)	0.2176(3)	71(13)					
H111	0.9891(5)	0.6240(5)	0.4690(4)	141(23)					
H112	0.9500(5)	0.5272(5)	0.4121(4)	141(23)					
H113	0.8806(5)	0.5565(5)	0.4791(4)	141(23)					
H13	0.6748(3)	1.0345(2)	0.2942(2)	93(10)					
H14	0.6792(3)	1.1446(2)	0.1826(2)	93(10)					
H15	0.7122(3)	1.0636(2)	0.0642(2)	93(10)					
H16	0.7408(3)	0.8724(2)	0.0574(2)	93(10)					
H17	0.7364(3)	0.7624(2)	0.1691(2)	93(10)					
H19	0.7037(3)	0.7951(3)	0.4716(2)	82(10)					
H20	0.5533(3)	0.8186(3)	0.5450(2)	82(10)					
H21	0.3751(3)	0.8841(3)	0.4838(2)	82(10)					
H22	0.3473(3)	0.9261(3)	0.3491(2)	82(10)					
H23	0.4977(3)	0.9025(3)	0.2758(2)	82(10)					
H25	0.8387(3)	0.4400(3)	0.2923(2)	143(14)					
H26	0.7861(3)	0.2571(3)	0.3137(2)	143(14)					
H27	0.6356(3)	0.2204(3)	0.3848(2)	143(14)					
H28	0.5376(3)	0.3666(3)	0.4344(2)	143(14)					
H29	0.5901(3)	0.5495(3)	0.4129(2)	143(14)					

cell constants were determined from 25 strong, carefully-centered reflections. The intensities were measured using the $\theta-2\theta$ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of data collection and they did not show any significant deviations from the initial measurements. Data decoding was accomplished using a locally written program. Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_o|$. No corrections for absorption were made due to the low value of the absorption coefficient (4.95 cm^{-1}). All data processing and calculations were carried out using the SHELX 76 system of programs [7]. The structure was solved by interpretation of the Patterson map which gave the position of the Mo atom. All the remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses. Since there was no reason to expect any abnormal distortions of the phenyl and the (η^5-C_5H_5) rings, they were refined as rigid bodies with idealised hydrogens. The methyl groups were treated in the same manner. The remaining atoms were refined anisotropically (except for the hydrogens) with refinement converging to the agreement factor listed in Table I. The scattering curves of Cromer and Mann [8] were used. Bond lengths, angles, least-squares planes presented in Tables III–V are based on the final positional parameters of Table II. The atomic numbering system is shown in Fig. 1. The labelling

TABLE III. Intramolecular Bond Distances (Å).

Mo–C1	2.386(7)
Mo–C2	2.307(7)
Mo–C3	2.300(7)
Mo–C4	2.374(7)
Mo–C5	2.426(7)
Mo–C6	1.941(11)
Mo–C7	2.007(11)
Mo–C8	2.353(8)
Mo–N1	2.160(7)
C6–O1	1.168(10)
C7–O2	1.115(11)
N1–C11	1.486(10)
N1–C9	1.294(10)
C9–N2	1.352(10)
N2–C10	1.471(9)
N2–C8	1.500(10)
C8–C12	1.533(10)
C8–C18	1.550(8)
C9–C24	1.476(9)
Mo–Cent*	2.026(7)
Cp(ideal)	1.420
Phen (ideal)	1.395
C–H (ideal)	0.95

*Cent = The geometric center of the Cp ring.

scheme of the hydrogens is such that its numbers are identical to that of the carbons they are attached to. The stereodrawings were obtained by using Johnson's ORTEP2 [9].

Results and Discussion

The compound exists in the crystal as discrete molecules in which the (Cp)(CO)$_2$Mo fragment is attached to a bidentate ligand having a nitrogen (N1) and a carbon (C8) as donor atoms and forming a five-membered chelate ring.

On the assumption that the (η^5-C$_5$H$_5$) = Cp ligand can be counted as a single binding point to the metal, the coordination polyhedron around the Mo atom is a square pyramid. Distortions from the theoretical geometry are due to the formation of the five membered chelate ring and also to the differences between the Mo–N, Mo–C and Mo–C(CO) bond lengths (Mo–N1 = 2.160(7); Mo–Cl = 2.386(7), Mo–C(CO) = 1.941(11), 2.007(11) and Mo–Cent (center of the Cp ring) = 2.026(7) Å. Atoms C6, C7, N1 and C8 which form the basal plane are only approximately planar having deviations as high as 0.14 Å from the least-squares plane defined by these atoms. The Cp and basal planes are almost parallel, the angle between them being 5.1°. The

TABLE IV. Intramolecular Bond Angles (°).

C6–Mo–C7	74.3(2)
C6–Mo–C8	115.9(2)
C6–Mo–N1	83.1(2)
C7–Mo–C8	78.2(2)
C7–Mo–N1	130.4(2)
C8–Mo–N1	73.0(2)
Mo–C8–N2	104.7(5)
C8–N2–C9	117.0(7)
N2–C9–N1	118.4(8)
C9–N1–Mo	120.0(6)
Mo–C8–C12	105.4(4)
Mo–C8–C18	118.4(4)
N2–C8–C12	111.0(5)
N2–C8–C18	103.5(5)
C12–C8–C18	113.5(5)
C8–N2–C10	118.6(7)
C9–N2–C10	120.8(7)
N2–C9–C24	118.6(7)
N1–C9–C24	123.0(8)
C9–N1–C11	119.4(8)
Mo–N1–C11	120.5(5)
Mo–C6–O1	178.4(9)
Mo–C7–O2	176.1(9)
C6–Mo–Cent*	120.8(2)
C7–Mo–Cent	118.3(2)
N1–Mo–Cent	111.3(2)
C8–Mo–Cent	123.2(2)

*Cent = The center of the Cp ring.

TABLE V. Least Squares Planes, Out-of-Plane Distances and Dihedral Angles.

A. C1–C5

$0.853x + 0.146y - 0.500z - 8.532 = 0$

Mo	−2.022

B. C12–C17

$-0.955x - 0.133y - 0.265z + 9.876 = 0$

C. C18–C23

$-0.270x - 0.939y - 0.211z - 12.655 = 0$

D. C24–C29

$-0.528x + 0.021y - 0.849z + 8.935 = 0$

E. Mo, N1, N2, C8, C9

$0.557x - 0.126y - 0.821z + 1.289 = 0$

Mo	0.114	C10	0.250
N2	−0.106	C11	−0.330
N2	0.181	C12	0.841
C8	−0.175	C18	−1.605
C9	−0.014	C24	−0.160

F. C6, C7, N1, C8

$0.807x + 0.134y - 0.575z - 4.461 = 0$

C6	−0.140	N1	0.123
C7	0.137	C8	−0.121
Mo	0.995	Cent	3.010

(continued overleaf)

TABLE V. *(continued)*

Dihedral Angles:

A	B	134.6°	E	B	107.3°
A	C	105.2	E	C	81.9
A	D	91.3	E	D	66.4
A	E	29.8	E	F	25.2
A	F	5.1			

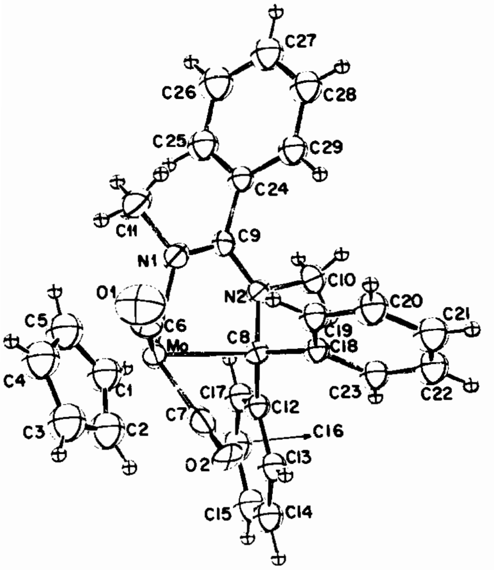


Fig. 1. A view of the molecule showing the atom labelling scheme used during the crystallographic study. These labels correspond to those used for the fractional coordinates listed in Table II.

distances of the Mo atom from the Cp and basal planes are 2.022 and 0.995 Å, respectively.

Table VI compares the geometry of the (Cp)Mo-$(CO)_2$ fragment bonded to various bidentate ligands containing five membered chelate rings. The coordination polyhedron around the Mo atom is a distorted square pyramid for all the examples listed. The similarity between the various parameters presented for three different compounds proves that the geometry of the (Cp)Mo$(CO)_2$ moiety remains largely undisturbed when changing the binding atoms of the bidentate ligand. The Mo–C(CO) distances of compound (C) are 2.007(11) and 1.941(11) Å while the corresponding C–O distances are 1.115(11) and 1.168(11) Å, respectively. As might be expected the shorter C–O bond is associated with the longer Mo–C(CO) distance. The difference of 0.07 Å between the two Mo–C(CO) distances is significant and may be the result of the *trans* effect. A similar effect was

TABLE VI. Comparison between the Geometry of the (Cp)Mo$(CO)_2$ Moiety in Various Square Pyramidal Compounds.

	The Compound	Mo–C(Cp)[a]	Mo–Cp	Mo–Basal Plane	Mo–N	Mo–C(CO)	C–O	OC–Mo–CO	S–Mo–N N–Mo–N C–Mo–N	Ref.
(A)	$[(C_5H_5)Mo(CO)_2NN^*]PF_6$ NN* = Schiff Base	2.345(25)	2.005	0.948	2.182(19)[b] 2.258(10)	1.984(14) 1.988(14)	1.120(18) 1.136(17)	73.5(6)	74.0(4)	13
(B)	$(C_5H_5)Mo(CO)_2[(C_5H_5N)C(=S)NR]$ H_2NR = phenylethylamine	2.355(23)	2.007	0.991	2.233(8)	1.929(14) 2.011(12)	1.164(17) 1.113(15)	76.6(5)	76.9(2)	14
(C)	$(C_5H_5)Mo(CO)_2[C(C_6H_5)N(CH_3)C(C_6H_5)N(CH_3)]$	2.359(24)	2.022	0.995	2.160(7)	1.941(11) 2.007(11)	1.168(10) 1.115(11)	74.3(2)	73.0(2)	This study

[a] Mean value and standard deviation of the mean. [b] Mo–N (imine bond is listed first).

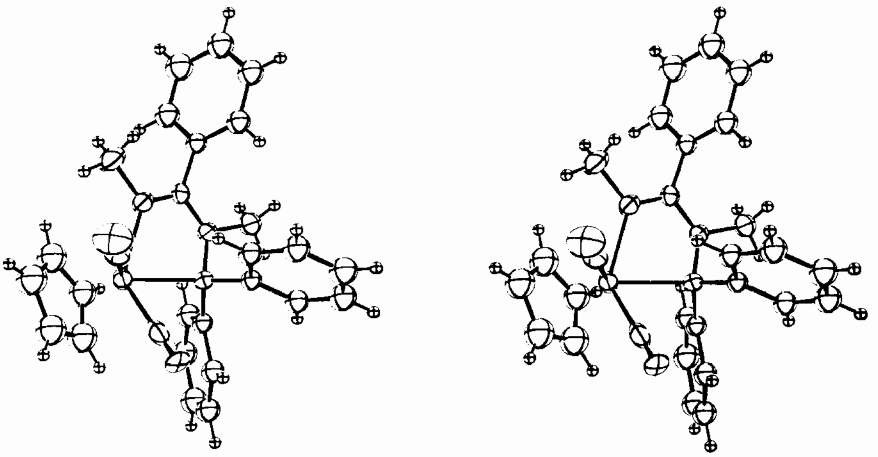


Fig. 2. Stereoscopic view of the molecule. The non-hydrogen atoms are shown with 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameters.

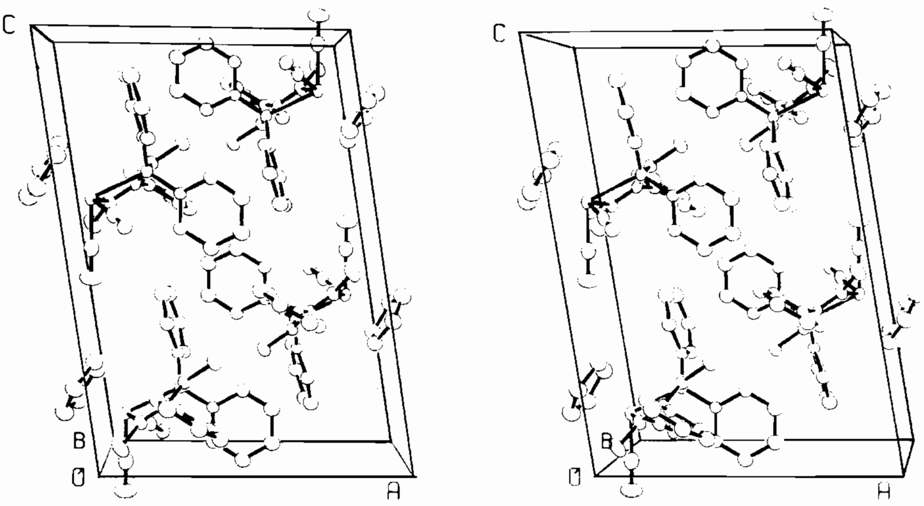


Fig. 3. Stereoscopic view of the molecular packing in the crystal lattice. The hydrogens were omitted for clarity.

observed also for compound (B). As usual with metal carbonyls the Mo–C–O angles deviate slightly from linearity with values of 178.4(9) and 176.1(9)°.

The chelate ring formed by atoms Mo, N1, N2, C8 and C9 is approximately planar, having deviations up to 0.18 Å from the least-squares plane defined by these atoms. The angle between the chelate plane and the basal plane of the square pyramid is 25.2°. The bite of the bidentate ligand produces an angle at Mo of 74.3(2)°. This value is close to that of 73.5(6)° observed for the corresponding N–Mo–N angle in compound (A) and to that of 76.6(5)° found for the N–Mo–S opening in compound (B). All these values are significantly higher than the value of 63.8(1)° observed for the bite of a thioamide ligand which results in the formation of a four-membered chelate ring. The Mo–N distance of 2.160(7)° is close to that observed in compounds (A) and (B). The distance from Mo to the carbon of the bidentate ligand, Mo–C8, is 2.353(8) Å, which is only slightly higher than that found in $[Mo_2(CH_3)_8]^{4-}$ [10] where the Mo–C bonds have a mean length of 2.29 Å (with individual values ranging from 2.27(1) to 2.31(1) Å). The C8–N2 distance of 1.500(10) is virtually identical to the value of 1.495(3) found by Mikhail for a pure single N–C bond [11].

The N1–C9 and N2–C9 bonds differ slightly, having values of 1.29(1) and 1.35(1) Å respectively. This slight but significant difference between the two C–N bonds suggests a somewhat uneven distribution or π-electron density between the two C–N bonds. The value of 1.476(9) Å observed for the C9–C24 bond is identical to the values expected for a carbon–carbon sp^2–sp^2 bond (1.477 Å) [12]. The C8–C12 and C8–C18 bonds are 1.533(10) and 1.550(8) Å, respectively, and are consistent with sp^3 carbon–sp^2 carbon distances.

The molecular conformation of the complex is such that the two aromatic groups (Cp and phenyl C12–C17 attached α to the Mo) are oriented close to an edge-to-face arrangement, with an interplanar angle of 134.6° and with a centroid-centroid distance of about 5 Å. This conformation leads to individual H(Cp)–C(Ph) contacts of around 2.6 Å (H1–C17 = 2.599(9) Å).

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References

1 H. Brunner, H. Schwagerl, J. Wachter, G. M. Reisner and I. Bernal, *Angew. Chem., 90,* 478 (1978) internat. Ed. 17, 453 (1978).
2 J. Wachter, private communication.
3 R. D. Adams, D. F. Chodosh and N. M. Golembski, *J. Organomet. Chem., 139,* C39 (1977).
4 P. B. Hitchcock, M. F. Lappert, G. M. McLaughlin and A. J. Oliver, *J. Chem. Soc. Dalton,* 68 (1974).
5 (a) H. Brunner, J. Wachter, I. Bernal and M. W. Creswick, *Angew. Chem., 91,* 920 (1979); *Internat. Ed., 18,* 861 (1979).
(b) G. M. Reisner and I. Bernal, *Inorg. Chim. Acta, 51,* 201 (1981).
6 J. Wachter, H. Brunner, I. Bernal and G. M. Reisner, *J. Organomet. Chem.,* to be submitted.
7 G. M. Sheldrick, 1976, private communication.
8 D. Cromer and J. Mann, *Acta Cryst., A24,* 321 (1974).
9 C. K. Johnson, 'ORTEP2, A Fortran-Ellipsoid Plot Program for Crystal Structure Illustration, ORNL-5138, Oak Ridge, Tenn., 1972.
10 F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson and G. Wilkinson, *J. Am. Chem. Soc., 96,* 3824 (1974).
11 I. Mikhail, *Acta Cryst., B33,* 1317 (1977).
12 D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc. London, Ser. A,* 270 (1960).
13 I. Bernal, S. J. LaPlaca, J. Korp, H. Brunner and W. Herrmann, *Inorg. Chem., 17,* 382 (1978).
14 G. M. Reisner and I. Bernal, *J. Organomet. Chem., 173,* 53 (1979).