Inorganica Chimica Acta, 51 (1981) 201–211

Ring Contraction in the Reaction of Cationic (h^5-C_5H_5)Mo(CO)$_2$(Schiff Base Chelate) Complexes with Methyl and Phenyl Lithium

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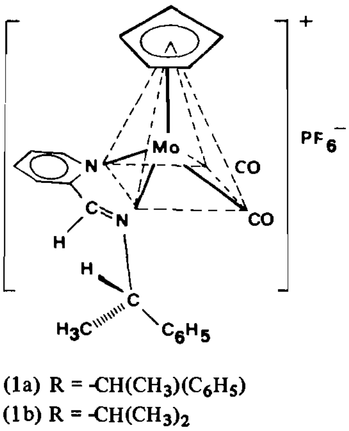
Received February 14, 1981

The crystal structures of $(C_5H_5)Mo(CO)_2(NHR)[C(NC_5H_4)R']$ *with* $R = -CH(CH_3)(C_6H_5)$, $R' = -CH_3$*(I) and* $R = -CH(CH_3)_2$, $R' = -(C_6H_5)$*(II) have been determined from single crystal X-ray diffraction data. The first compound crystallizes in the monoclinic space group* $P2_1/a$ *with* a = *17.053(9),* b = *11.185(5),* c = *11.011(3)* Å, β = *104.48(3)°; the second crystallizes in the orthorhombic space group* $P2_12_12_1$ *with* a = *8.477(3),* b = *14.132(7),* c = *16.670(8)* Å. *Both compounds are characterized by the existence of a three membered ring formed by a* n^2*-aminomethylene ligand bonded to the Mo through its C and N atoms. The coordination polyhedron around the Mo atom is a distorted square pyramid; the greatest deviation from the theoretical geometry being the N(1)–Mo–C(8) angle for which values of 37.6(4) and 38.0(2)° were observed. The orientation of the pyridine ring is determined by the formation of a strong intramolecular hydrogen bond between its nitrogen and the N(1)–H(6) hydrogen of the aminomethylene moiety.*

Introduction

In the reaction between C_6H_5Li and $[(C_5H_5)Mo(CO)_2NN']PF_6$ (NN′ = Schiff base derived from 2-pyridinecarbaldehyde and (*S*)-1-phenylethylamine) a stereospecific phenyl addition at the azomethine carbon was supposed to occur [1]. In order to test this assumption, X-ray structure determinations of crystals derived from the reaction of cationic pyridinecarbaldimine complexes (1) with C_6H_5Li and CH_3Li were undertaken.



(1a) R = $-CH(CH_3)(C_6H_5)$
(1b) R = $-CH(CH_3)_2$

We now report the structure of two of the compounds derived from the reaction of (1a) with CH_3Li and of (1b) with C_6H_5Li. The two compounds will henceforth be referred as (I) and (II).

Experimental

The details of the synthesis and the physical properties of the compounds have been reported elsewhere [2]. X-ray data collection for compounds (I) and (II) involved similar procedures. Intensity measurements were made on an ENRAF-NONIUS CAD-4 computer controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing is given in Table I. Accurate cell constants determination and data collection methods were similar to those described elsewhere [3] and are, thus, not reported here.

Solution and Refinement

Data decoding was accomplished using a locally written program (J. D. Korp, Houston). Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_o|$. No absorption corrections were made due to the low value of the absorption coefficients. Standard deviations of the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{TOT} + 2\Sigma I_{BG}$. Standard deviations in the structure factors amplitudes, $\sigma(|F_o|)$, were estimated as $\sigma(|F_o|) = \sigma(I)/2Lp|F_o|$. All data processing and calculations were carried out using the X-Ray 72 System of programs [4].

For both compounds, three dimensional Patterson maps were computed and the positions of the Mo atoms determined. All the remaining nonhydrogen atoms were easily found from successive difference

TABLE I. Crystallographically Important Data Collection and Data Processing Information for Crystals (I) and (II).

	Crystal (I)	Crystal (II)
Empirical Formula	$MoN_2O_2C_{22}H_{22}$	Same
Molecular Weight	442.35 gm mol^{-1}	Same
Cell Constants	a = 17.053(9) Å	a = 8.477(3) Å
	b = 11.185(5)	b = 14.132(7)
	c = 11.011(3)	c = 16.670(8)
	β = 104.48(3)°	
Unit Cell Volume	V = 2033.5 Å^3	1997.0 Å^3
Space Group	$P2_1/a$	$P2_12_12_1$
Density	ρ(calc.) = 1.445 gm cm^{-3}	1.471 gm cm^{-3}
Radiation Used for Data Collection	MoK$_\alpha$ (λ = 0.71069 Å)	Same
Absorption Coefficient	μ = 6.5 cm^{-1}	6.6 cm^{-1}
Scanning Range for 2θ	$3.00° < 2\theta < 60.0°$	$4.00° < 2\theta < 60.0°$
Crystal along	[1, 0, $\bar{1}$]	[0, 1, 0]
Standards for Intensity Control	[6, 4, 1 and $\bar{6}$, $\bar{4}$, $\bar{1}$]	[$\bar{4}$, $\bar{2}$, 2 and $\bar{4}$, 2, $\bar{4}$]
Scan Width for each Reflection	$\Delta\theta = (0.80 + 0.35 \tan\theta)°$	$\Delta\theta = (1.00 + 0.35 \tan\theta)°$
Maximum Scan Time	5 minutes	4 minutes
Minimum Number of Counts above Background for each Reflection	2000	Same
Scan Technique	$\theta - 2\theta$	Same
Total Number of Reflections Collected[a]	6364	4748
Number of Contributing Reflections in the last Least-Squares[b]	3268	3589
Number of Variables	332	Same
Weighting Scheme	$w = 1/\sigma^2(Fo)$	Same
Final R(F)[c]	0.054	0.051
Final R$_w$(F)[d]	0.057	0.057

[a] For crystal (I) a total of 6364 reflections were collected on which 1269 having $I > 3\sigma(I)$ were classified as 'observed' with the remaining 5095 being termed 'less-thans.' For crystal (II), 2736 reflections were classified 'observed' and 2012 'less-thans.' [b] 1269 'observed' and 1999 'less-thans,' for which $|F_c| > |F_o|$ for crystal (I) and 2736 'observed' and 853 'less-thans' for crystal (II). [c] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [d] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Fourier maps. The nitrogen atom of the pyridine ring was identified by means of its temperature factor (refinement of the six pyridine atoms as carbons resulted in a low temperature factor of one of the sites), by the absence of any residual electron density in the vicinity of the assumed nitrogen which might be identified as a hydrogen and by the formation of a hydrogen bond to the N(1)–H(6) group (see refinement and discussion). Full-matrix least-squares refinement with isotropic motion for all the nonhydrogen atoms was followed by anisotropic refinement. At this stage hydrogen atoms were added at theoretically calculated positions (C–H = 0.95 Å). Further anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogens (for (I)) yielded the following final unweighted and weighted agreement factors; R(F) = 0.054, R_w = 0.057 and R = 0.051, R_w = 0.057 for crystals (I) and (II), respectively. The function minimized during all the least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$, where w, the weighting factors, were $[\sigma(|F_o|)]^{-2}$. The atomic scattering curves of Cromer and Mann [5] were used for the nonhydrogen atoms and, for the hydrogen atoms the curve of Stewart *et al.* [6] was used. Corrections for the real and imaginary terms of the anomalous dispersion for Mo were applied for compound (II). For (I) only the real part of the anomalous scattering for Mo was used. The values used for these corrections were those given by the International Tables for X-ray Crystallography [7]. The estimated standard deviations were computed from the inverse matrix of the final least squares cycle. Final positional and thermal parameters for compound (I) are presented in Tables IIa, IIIa and IVa, and for compound (II) in Tables IIb, IIIb and IVb. Interatomic distances and angles are given in Tables Va, VIa and Vb, VIb for compounds I and II, respectively. The equations of the least squares planes through selected groups of atoms are given in Tables VIIa and VIIb. The stereo drawings for compound (I) (Figs. 1, 2, 3) and for compound (II) (Figs. 4, 5, 6) were obtained by using Johnson's ORTEP2 [8]. Final observed and calculated structure factors are available from either the Editor of this journal or from the authors.

Determination of the absolute configuration of compound (II)

When refinement converged, the molecular configuration was that given in Figs. 4–6. A check of

TABLE IIa. Final Positional Parameters of the Non-Hydrogen Atoms for Crystal (I).

Atom[a]	X	Y	Z
Mo	0.29631(7)	0.24134(11)	0.18021(9)
N(1)	0.3791(5)	0.3853(7)	0.2607(8)
C(1)	0.2638(10)	0.0373(12)	0.2021(15)
C(2)	0.2032(10)	0.1054(16)	0.2273(19)
C(3)	0.2332(15)	0.1714(14)	0.3331(20)
C(4)	0.3189(13)	0.1456(14)	0.3798(14)
C(5)	0.3376(10)	0.0590(13)	0.2944(15)
C(6)	0.2149(7)	0.3524(11)	0.0921(12)
C(7)	0.2993(8)	0.2147(12)	0.0081(11)
C(8)	0.4159(7)	0.3200(10)	0.1793(10)
C(9)	0.4830(6)	0.2402(11)	0.2540(9)
C(10)	0.5218(7)	0.1581(11)	0.1933(12)
C(11)	0.5795(9)	0.0820(11)	0.2644(16)
C(12)	0.5949(10)	0.0899(14)	0.3965(16)
C(13)	0.5555(9)	0.1759(13)	0.4490(13)
N(2)	0.4983(6)	0.2493(10)	0.3794(8)
C(14)	0.4331(8)	0.3829(10)	0.0662(11)
C(15)	0.3619(7)	0.5167(9)	0.2468(10)
C(16)	0.3146(8)	0.5520(11)	0.3431(12)
C(17)	0.4364(7)	0.5946(9)	0.2594(10)
C(18)	0.5114(8)	0.5607(11)	0.3334(11)
C(19)	0.5794(8)	0.6346(12)	0.3422(13)
C(20)	0.5694(8)	0.7439(14)	0.2783(11)
C(21)	0.4937(9)	0.7784(12)	0.2066(12)
C(22)	0.4267(8)	0.7043(10)	0.1955(12)
O(1)	0.1632(6)	0.4125(8)	0.0321(9)
O(2)	0.2988(6)	0.2005(10)	−0.0962(8)

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

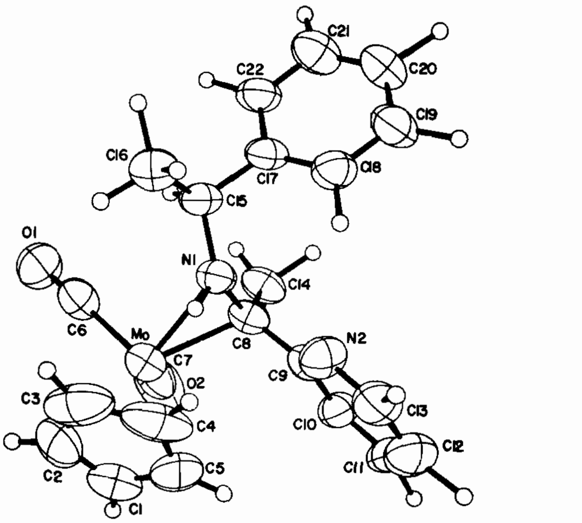


Fig. 1. A general view of compound (I) showing the labelling scheme used in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and of convenient size for the hydrogen atoms.

TABLE IIb. Final Positional Parameters of the Non-Hydrogen Atoms for Crystal (II).

Atom	X	Y	Z
Mo	0.01801(7)	0.06615(4)	0.24089(3)
N(1)	0.2603(7)	0.0377(4)	0.2768(3)
C(1)	0.0258(11)	0.0675(7)	0.0961(4)
C(2)	0.0458(12)	−0.0288(7)	0.1222(5)
C(3)	−0.0899(12)	−0.0552(6)	0.1629(5)
C(4)	−0.1970(11)	0.0173(7)	0.1648(5)
C(5)	−0.1259(11)	0.0986(7)	0.1239(5)
C(6)	−0.0572(9)	0.0124(6)	0.3404(4)
C(7)	−0.0784(10)	0.1755(6)	0.2909(5)
C(8)	0.2511(7)	0.1388(4)	0.2638(4)
C(9)	0.3156(8)	0.1657(5)	0.1827(4)
C(10)	0.2826(10)	0.2542(6)	0.1470(4)
C(11)	0.3396(11)	0.2743(6)	0.0715(5)
C(12)	−0.1091(8)	−0.0213(5)	0.3995(4)
C(13)	0.4554(10)	0.1210(6)	0.0707(4)
N(2)	0.4008(8)	0.1017(5)	0.1447(4)
C(14)	0.3193(10)	−0.0035(6)	0.3530(5)
C(15)	0.2854(13)	−0.1091(6)	0.3496(6)
C(16)	0.4982(11)	0.0138(6)	0.3609(6)
C(17)	0.2909(8)	0.2068(5)	0.3303(4)
C(18)	0.4213(10)	0.2650(6)	0.3226(5)
C(19)	0.4632(11)	0.3317(7)	0.3837(5)
C(20)	0.3769(12)	0.3347(7)	0.4542(5)
C(21)	0.2495(13)	0.2733(7)	0.4646(5)
C(22)	0.2053(10)	0.2102(6)	0.4028(4)
O(1)	−0.1091(8)	−0.0213(5)	0.3995(4)
O(2)	−0.1431(10)	0.2413(6)	0.3199(5)

F(hkl) calculated for that absolute configuration and its enantiomer showed 9 reflections suitable for the Bijvoet test [9]. These reflections were measured, each four times, using the diffractometer routine MODE = −1 [10] in the order hkl, $\overline{hkl}$, $\overline{hkl}$, hkl, hkl, $\overline{hkl}$, $\overline{hkl}$, hkl, and the four independently measured values were then averaged. The results are given in Table VIII, where it is shown that the coordinates initially chosen and used for Figs. 4–6 correspond to those of the correct enantiomer. Since there are two identical carbonyl groups, we define arbitrarily the third ranking ligand as being C(6) (*cis* to the 2nd ranking atom, N(1)). Thus, using the extension of the R, S system [11] to polyhapto ligands in organometallic complexes [12], the priority sequence of the ligands is C_5H_5 > N(1) > C(6). According to the rule of the R, S system and the line of sight convention previously described [13] the configuration at the Mo atom is (*S*). The relationship between this configuration, that of the parent compound and their signs of optical rotation will be described in a subsequent paper [14]. It is clear that the choice of symbol to define the absolute configuration at Mo in this substance is the same regardless of which carbonyl ligand is used since they are both on the same side of N(1) with respect to the line of sight of the observer [13].

TABLE IIIa. Final Positional Parameters of the Hydrogen Atoms[a] for Crystal (I).

Atom	X	Y	Z
H(1)	0.258	−0.016	0.133
H(2)	0.149	0.107	0.179
H(3)	0.203	0.225	0.370
H(4)	0.355	0.179	0.452
H(5)	0.389	0.023	0.299
H(6)	0.416(7)	0.366(11)	0.363(11)
H(10)	0.513(8)	0.156(13)	0.089(13)
H(11)	0.611(7)	0.016(10)	0.222(10)
H(12)	0.649(11)	0.040(16)	0.459(17)
H(13)	0.561(7)	0.189(11)	0.561(12)
H(141)	0.487(10)	0.431(14)	0.090(14)
H(142)	0.431(5)	0.324(8)	0.003(8)
H(143)	0.386(13)	0.451(18)	0.032(19)
H(15)	0.329(7)	0.524(10)	0.141(10)
H(161)	0.264(7)	0.497(11)	0.325(11)
H(162)	0.344(8)	0.533(12)	0.434(12)
H(163)	0.305(9)	0.647(15)	0.355(15)
H(18)	0.514(8)	0.464(12)	0.391(12)
H(19)	0.643(9)	0.602(14)	0.413(14)
H(20)	0.632(9)	0.806(13)	0.299(14)
H(21)	0.477(9)	0.861(14)	0.146(14)
H(22)	0.362(7)	0.740(12)	0.130(10)

[a] The numbering system of the hydrogens is such that its number is identical to that of the carbon it is attached to. The positions of the Cp hydrogens are theoretical (calculated for C–H = 0.95 Å).

TABLE IIIb. Theoretical Positions of the Hydrogen Atoms[a] for Crystal (II).

Atom	X	Y	Z
H(1)	0.0993	0.1038	0.0660
H(2)	0.1359	−0.0673	0.1131
H(3)	−0.1064	−0.1156	0.1864
H(4)	−0.2990	0.0152	0.1883
H(5)	−0.1711	0.1596	0.1172
H(6)	0.3264	0.0135	0.2356
H(10)	0.2212	0.2997	0.1751
H(11)	0.3202	0.3339	0.0470
H(12)	0.4671	0.2134	−0.0214
H(13)	0.5168	0.0741	0.0444
H(14)	0.2662	0.0243	0.3973
H(151)	0.1752	−0.1198	0.3447
H(152)	0.3385	−0.1369	0.3053
H(153)	0.3232	−0.1355	0.3984
H(161)	0.5512	−0.0151	0.3171
H(162)	0.5183	0.0799	0.3606
H(163)	0.5360	−0.0126	0.4097
H(18)	0.4845	0.2606	0.2757
H(19)	0.5495	0.3735	0.3759
H(20)	0.4043	0.3783	0.4953
H(21)	0.1922	0.2739	0.5136
H(22)	0.1171	0.1697	0.4102

[a] The numbering system of the hydrogens is such that its number is identical to that of the carbon it is attached to. H(6) is bonded to N(1). The positions of the hydrogens are theoretical (calculated for C–H = 0.95 Å).

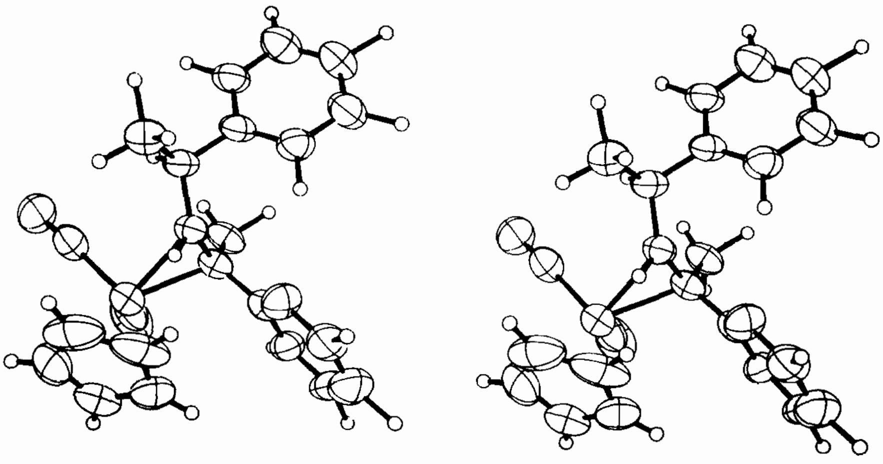
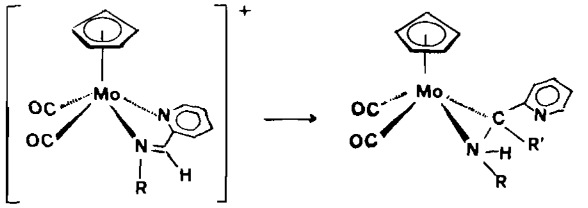


Fig. 2. A stereo pair of molecule (I).

Results and Discussion

Crystal structure determinations of compounds (I) and (II) surprisingly show that during the reaction between the cationic $[(n^5\text{-}C_5H_5)Mo(CO)_2$ (Schiff base)] complex with methyl or phenyl lithium, a contraction of the five membered chelate system present in the parent substances occurs, leading to the formation of a n^2-aminomethylene ligand bonded to the Mo through its C and N atoms. This rearrangement can formally be considered as an exchange of CH_3 or C_6H_5 for the H at the azomethine carbon, addition of H to the imine nitrogen, cleavage of the Mo–N(pyridine) bond and formation of a Mo–C bond to give a three membered ring:



(I) R = -CH(CH$_3$)(C$_6$H$_5$) R' = -CH$_3$
(II) R = -CH(CH$_3$)$_2$ R' = -C$_6$H$_5$

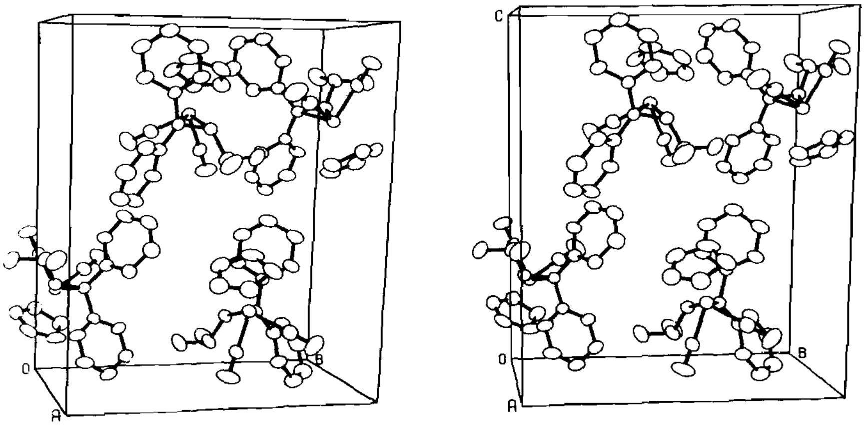


Fig. 3. A packing diagram of compound (I).

TABLE IVa. Thermal Parameters (× 10^3)[a] of the Non-Hydrogen Atoms for Crystal (I).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	61.2(9)	56.2(9)	55.2(8)	−6.0(5)	14.9(5)	−0.7(5)
N(1)	57(5)	43(5)	53(5)	−4(4)	15(4)	0(4)
C(1)	104(12)	54(8)	103(11)	−12(8)	36(10)	6(8)
C(2)	86(11)	90(12)	142(16)	−21(10)	44(11)	31(12)
C(3)	183(21)	55(9)	121(15)	11(12)	95(16)	21(10)
C(4)	158(17)	57(9)	66(9)	−30(11)	8(10)	16(7)
C(5)	100(12)	57(8)	106(12)	7(8)	23(10)	33(8)
C(6)	63(8)	69(8)	68(8)	−13(7)	8(6)	3(6)
C(7)	69(8)	86(10)	66(7)	−28(7)	14(6)	−19(7)
C(8)	63(7)	49(6)	49(6)	12(6)	15(5)	−9(5)
C(9)	54(6)	48(6)	55(6)	−9(6)	14(5)	0(5)
C(10)	61(8)	52(7)	74(8)	7(6)	26(6)	4(6)
C(11)	79(10)	48(7)	126(13)	16(7)	43(10)	15(8)
C(12)	87(11)	71(10)	105(12)	4(9)	24(10)	26(9)
C(13)	83(10)	67(9)	78(9)	−6(8)	−5(8)	20(7)
N(2)	75(7)	63(6)	52(5)	11(6)	5(5)	10(5)
C(14)	84(9)	56(7)	54(6)	−22(7)	24(6)	−8(5)
C(15)	71(8)	39(6)	47(6)	3(5)	3(5)	−4(4)
C(16)	82(9)	56(7)	67(8)	1(7)	19(7)	−3(6)
C(17)	68(8)	38(6)	55(6)	−4(5)	10(6)	−9(5)
C(18)	69(8)	51(7)	65(7)	1(6)	6(6)	4(6)
C(19)	79(10)	64(8)	81(9)	−17(8)	9(7)	−11(7)
C(20)	77(9)	69(8)	64(7)	−26(8)	12(7)	−3(7)
C(21)	92(11)	67(9)	68(8)	−17(8)	15(8)	3(7)
C(22)	73(8)	41(6)	77(8)	−3(6)	8(7)	1(6)
O(1)	76(6)	82(6)	88(7)	7(5)	7(5)	21(5)
O(2)	115(8)	137(10)	61(5)	−46(7)	27(6)	−29(6)

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

TABLE IVb. Thermal Parameters (× 10^3) of the Non-Hydrogen Atoms for Crystal (II).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	35.5(2)	35.8(2)	27.7(2)	−1.3(2)	−1.8(2)	2.3(2)
N(1)	38(3)	36(3)	27(2)	4(2)	0(2)	0(2)
C(1)	61(5)	72(5)	28(3)	−9(6)	−5(3)	1(3)
C(2)	66(6)	58(5)	43(4)	1(5)	−2(4)	−18(4)
C(3)	80(6)	49(4)	44(4)	−17(5)	−11(4)	−3(4)
C(4)	52(5)	67(6)	44(4)	−11(5)	−11(4)	−3(4)
C(5)	56(5)	72(6)	41(4)	−3(5)	−21(4)	13(4)
C(6)	38(4)	50(4)	36(3)	−3(3)	−1(3)	7(3)
C(7)	46(4)	47(4)	42(4)	3(4)	−9(3)	0(3)
C(8)	36(3)	32(3)	27(2)	0(2)	0(3)	3(2)
C(9)	36(4)	38(3)	25(2)	0(3)	1(2)	4(2)
C(10)	50(4)	47(4)	30(3)	−7(4)	1(3)	8(3)
C(11)	60(5)	51(5)	35(4)	−15(4)	−6(4)	11(3)
C(12)	54(5)	67(5)	30(3)	−10(4)	4(3)	10(3)
C(13)	50(5)	63(5)	34(3)	2(4)	8(3)	−2(3)
N(2)	46(4)	54(4)	31(3)	10(3)	6(3)	8(3)
C(14)	45(4)	41(4)	38(3)	9(3)	−6(3)	12(3)
C(15)	67(6)	48(4)	62(6)	11(5)	1(5)	23(4)
C(16)	46(5)	60(5)	83(6)	0(5)	−20(5)	29(4)
C(17)	31(3)	43(3)	30(3)	−1(3)	−3(3)	1(3)
C(18)	42(4)	55(5)	41(4)	−4(4)	−6(3)	4(3)
C(19)	52(5)	66(5)	53(5)	−15(5)	−17(4)	0(4)
C(20)	68(6)	64(5)	42(4)	−3(5)	−17(4)	−10(4)
C(21)	70(6)	66(6)	33(4)	−4(5)	−6(4)	−10(4)
C(22)	51(5)	52(4)	29(3)	−3(4)	1(3)	−2(3)
O(1)	63(4)	79(4)	39(3)	−13(4)	7(3)	16(3)
O(2)	82(5)	84(5)	74(5)	33(5)	−5(4)	−27(4)

TABLE Va. Bond Distances (Å) with Estimated Standard Deviations in Parentheses for Crystal (I).

Mo–N(1)	2.178(8)
Mo–C(1)	2.374(14)
Mo–C(2)	2.348(19)
Mo–C(3)	2.348(25)
Mo–C(4)	2.388(15)
Mo–C(5)	2.407(15)
Mo–C(6)	1.933(12)
Mo–C(7)	1.932(13)
Mo–C(8)	2.223(12)
C(1)–C(2)	1.367(25)
C(2)–C(3)	1.366(27)
C(3)–C(4)	1.451(32)
C(4)–C(5)	1.441(24)
C(1)–C(5)	1.426(21)
N(1)–C(8)	1.418(16)
C(8)–C(9)	1.521(15)
C(9)–C(10)	1.395(18)
C(10)–C(11)	1.385(18)
C(11)–C(12)	1.415(25)
C(12)–C(13)	1.381(24)
C(13)–N(2)	1.356(17)
N(2)–C(9)	1.344(13)
C(8)–C(14)	1.521(17)
N(1)–C(15)	1.499(13)
C(15)–C(16)	1.536(19)
C(15)–C(17)	1.519(17)
C(17)–C(18)	1.387(16)
C(18)–C(19)	1.408(20)
C(19)–C(20)	1.400(20)
C(20)–C(21)	1.388(18)
C(21)–C(22)	1.392(20)
C(22)–C(17)	1.403(16)
C(6)–O(1)	1.172(15)
C(7)–O(2)	1.157(16)
N(1)–N(2)	2.613(13)

TABLE Vb. Bond Distances (Å) for Crystal (II).

Mo–N(1)	2.177(6)	C(11)–C(12)	1.419(13)
Mo–C(1)	2.415(7)	C(12)–C(13)	1.357(12)
Mo–C(2)	2.402(9)	C(13)–N(2)	1.345(10)
Mo–C(3)	2.339(9)	N(2)–C(9)	1.319(10)
Mo–C(4)	2.326(9)	C(8)–C(17)	1.506(10)
Mo–C(5)	2.346(9)	C(17)–C(18)	1.383(11)
Mo–C(6)	1.932(8)	C(18)–C(19)	1.433(13)
Mo–C(7)	1.937(8)	C(19)–C(20)	1.385(13)
Mo–C(8)	2.259(6)	C(20)–C(21)	1.396(15)
C(1)–C(2)	1.438(13)	C(21)–C(22)	1.413(12)
C(2)–C(3)	1.387(14)	C(22)–C(17)	1.411(10)
C(3)–C(4)	1.369(14)	N(1)–C(14)	1.484(10)
C(4)–C(5)	1.466(14)	C(14)–C(15)	1.522(12)
C(1)–C(5)	1.426(13)	C(14)–C(16)	1.542(13)
N(1)–C(8)	1.446(8)	C(6)–O(1)	1.180(10)
C(8)–C(9)	1.508(9)	C(7)–O(2)	1.183(12)
C(9)–C(10)	1.413(10)	N(1)–N(2)	2.662(8)
C(10)–C(11)	1.378(11)		

TABLE VIa. Angles (°) with Estimated Standard Deviations in Parentheses for Crystal (I).

N(1)–Mo–C(8)	37.6(4)
N(1)–Mo–C(6)	92.3(4)
N(1)–Mo–C(7)	109.9(5)
C(6)–Mo–C(7)	78.4(6)
C(6)–Mo–C(8)	106.7(5)
C(7)–Mo–C(8)	78.9(5)
C(2)–C(1)–C(5)	109.8(1.4)
C(1)–C(2)–C(3)	109.4(1.6)
C(2)–C(3)–C(4)	108.9(1.8)
C(3)–C(4)–C(5)	105.7(1.4)
C(4)–C(5)–C(1)	106.2(1.5)
Mo–N(1)–C(8)	72.9(6)
Mo–N(1)–C(15)	126.3(6)
C(8)–N(1)–C(15)	123.1(9)
Mo–C(8)–C(9)	109.4(7)
Mo–C(8)–C(14)	123.5(7)
Mo–C(8)–N(1)	69.5(6)
N(1)–C(8)–C(9)	110.7(9)
N(1)–C(8)–C(14)	119.0(9)
C(9)–C(8)–C(14)	116.1(1.0)
C(8)–C(9)–C(10)	120.7(9)
C(8)–C(9)–N(2)	115.9(1.0)
C(10)–C(9)–N(2)	123.2(1.0)
C(9)–C(10)–C(11)	119.3(1.2)
C(10)–C(11)–C(12)	117.7(1.4)
C(11)–C(12)–C(13)	119.3(1.3)
C(12)–C(13)–N(2)	122.8(1.3)
C(13)–N(2)–C(9)	117.6(1.1)
N(1)–C(15)–C(16)	107.7(9)
N(1)–C(15)–C(17)	114.6(9)
C(16)–C(15)–C(17)	111.2(9)
C(15)–C(17)–C(18)	121.6(1.0)
C(15)–C(17)–C(22)	117.7(1.0)
C(18)–C(17)–C(22)	120.7(1.1)
C(17)–C(18)–C(19)	120.1(1.1)
C(18)–C(19)–C(20)	118.9(1.2)
C(19)–C(20)–C(21)	120.5(1.3)
C(20)–C(21)–C(22)	120.7(1.2)
C(21)–C(22)–C(17)	119.0(1.1)
Mo–C(6)–O(1)	174.6(1.1)
Mo–C(7)–O(2)	177.9(1.1)

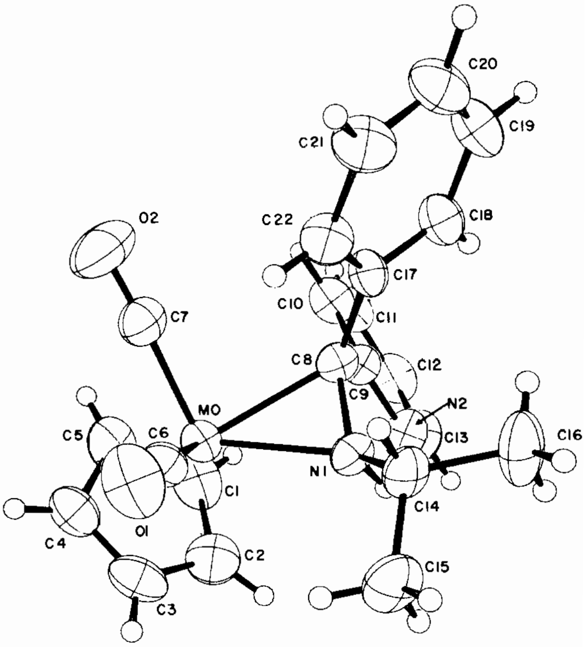


Fig. 4. A general view of compound (II) in its correct absolute configuration, showing the labelling scheme used in the crystallographic study.

The products have been investigated by I.R., ^1H and ^{13}C NMR spectra [2] and by a preliminary X-ray study [15]. These three membered ring compounds are similar to the complexes previously described by Fong and Wilkinson [16]. Abel *et al.* [17], studied the crystal structure of the aziridinyl-methylenetetracarbonyl manganese complex and suggested an essentially symmetric π-bonding of the aminomethylene ligand, rather than the alternative metal–nitrogen σ bonded arrangement. The shorter Mn–N distance was explained by enhanced π-donation to the nitrogen by the metal. The high π-acidity of the aminomethylene ligand is reflected in the N–C bond length which was found to correspond, within experimental error, to unit bond order. Bond lengths found

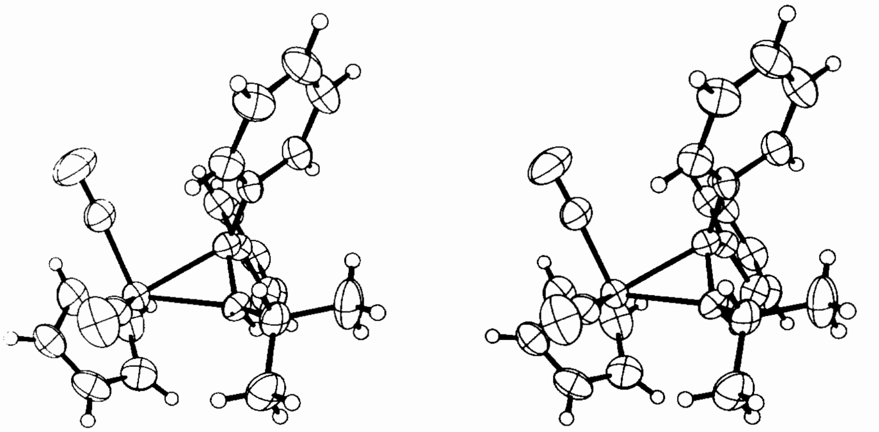


Fig. 5. A stereo pair of molecule (II) in its correct absolute configuration.

TABLE VIb. Angles (°) for Crystal (II).

N(1)–Mo–C(8)	38.0(2)	C(8)–C(9)–N(2)	117.2(6)
N(1)–Mo–C(6)	90.2(3)	C(10)–C(9)–N(2)	120.9(6)
N(1)–Mo–C(7)	115.3(3)	C(9)–C(10)–C(11)	119.8(7)
C(6)–Mo–C(7)	78.7(3)	C(10)–C(11)–C(12)	118.1(8)
C(6)–Mo–C(8)	108.8(3)	C(11)–C(12)–C(13)	117.9(7)
C(7)–Mo–C(8)	78.7(3)	C(12)–C(13)–N(2)	123.9(8)
C(2)–C(1)–C(5)	107.3(8)	C(13)–N(2)–C(9)	119.3(7)
C(1)–C(2)–C(3)	107.7(8)	N(1)–C(14)–C(15)	106.9(7)
C(2)–C(3)–C(4)	111.1(8)	N(1)–C(14)–C(16)	110.1(7)
C(3)–C(4)–C(5)	107.7(8)	C(15)–C(14)–C(16)	110.1(7)
C(4)–C(5)–C(1)	106.1(8)	C(8)–C(17)–C(18)	119.3(6)
Mo–N(1)–C(8)	74.1(3)	C(8)–C(17)–C(22)	122.5(6)
Mo–N(1)–C(14)	128.7(5)	C(18)–C(17)–C(22)	118.0(7)
C(8)–N(1)–C(14)	122.2(5)	C(17)–C(18)–C(19)	121.5(8)
Mo–C(8)–C(9)	106.3(4)	C(18)–C(19)–C(20)	119.5(9)
Mo–C(8)–C(17)	127.6(4)	C(19)–C(20)–C(21)	119.6(9)
Mo–C(8)–N(1)	67.9(3)	C(20)–C(21)–C(22)	120.4(8)
N(1)–C(8)–C(9)	111.3(5)	C(21)–C(22)–C(17)	120.7(8)
N(1)–C(8)–C(17)	120.5(6)	Mo–C(6)–O(1)	177.1(7)
C(21)–C(22)–C(17)	120.7(8)	Mo–C(7)–O(2)	177.2(8)
C(8)–C(9)–C(10)	121.9(6)		

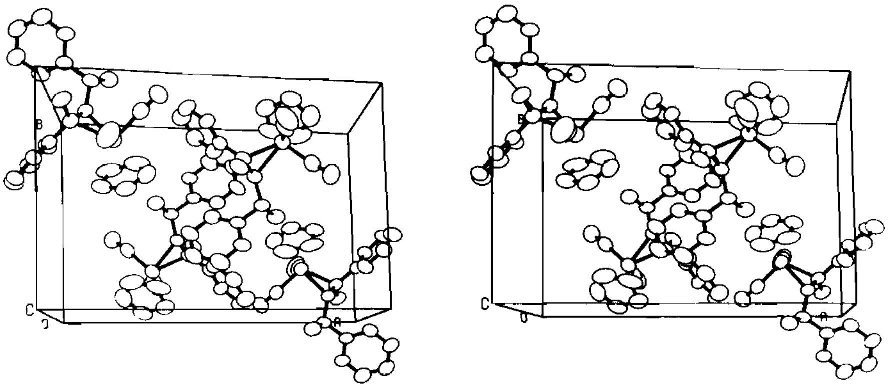


Fig. 6. A packing diagram of compound (II).

for compounds (I) and (II) are comparable with those reported by Abel *et al.* [17]. Thus, the Mo–N distances (2.178(8) and 2.177(6) Å) are shorter than the Mo–C bond lengths of 2.223(12) and 2.259(6) Å. The N–C bond distances were found to be close to the unit bond order with values of 1.418(16) and 1.446(8) Å.

On the assumption that the (n^2-C_5H_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 this geometry are mainly due to the formation of the three membered ring and also to the differences in the length between the Mo–N, Mo–C and Mo–C(O) bonds. The greatest deviation from the theoretical geometry was observed for the N(1)–Mo–C(8) angle which has values of 37.6(4) and 38.0(2)° for compounds (I) and (II), respectively. Atoms N(1), C(6), C(7) and C(8) which form the basal plane are only approximately planar having deviations as high as 0.12 Å from the least squares plane defined by these atoms. The Cp and basal planes are almost parallel, the angles between them being 5.94 and 8.77°. The distances of the Mo atom from the basal plane and from the Cp ring plane are, for compounds (I) and (II), respectively, 1.11, 2.05 Å and 1.07 and 2.03 Å.

In order to compare the geometry of the (n^5-C_5H_5)Mo(CO)$_2$ unit bonded to the n^2-aminomethylene ligands (compounds I and II) with that found in similar complexes, ([(C_5H_5)Mo(CO)$_2$-(NN*)]PF_6 with NN* being the Schiff base derived from pyridine-2-carbaldehyde and (*S*)-phenylethylamine, compound (III), and (C_5H_5)Mo(CO)$_2$-(C_4H_3N)–CH(=N–R*) with R* being (*S*)-CH)(CH_3)-(C_6H_5), compound (IV)), Table IX was prepared. It is observed that whereas the geometry of compounds (I) and (II) show a high degree of internal consistency, their molecular parameters differ from the other

TABLE VIIa. Least Squares Planes (in Orthogonal Å Space) and Deviation of Atoms from these Planes (in Å) for Crystal I.

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

$0.3717x + 0.7404y - 0.5600z = 0.5696$

C(1)	−0.0014	C(2)	0.0021
C(3)	−0.0018	C(4)	0.0009
C(5)	0.0003	Mo	2.0471

(b) Plane based on C(9), C(10), C(11), C(12), C(13), and N(2)

$0.7417x + 0.6707y - 0.0080z = 7.3732$

C(9)	−0.0021	C(10)	0.0009
C(11)	0.0085	C(12)	−0.0174
C(13)	0.0169	N(2)	−0.0068
C(8)	−0.0942	N(1)	−0.2430
		H(6)	−0.1411

(c) Plane based on C(17), C(18), C(19), C(20), C(21), and C(22)

$-0.4082x + 0.4480y + 0.7954z = 2.4400$

C(17)	−0.0066	C(18)	0.0121
C(19)	−0.0073	C(20)	−0.0030
C(21)	0.0086	C(22)	−0.0038

(d) Plane based on Mo, N(1) and C(8)

$0.2609x - 0.5971y + 0.7586z = 1.0346$

(e) Plane based on C(15), N(1), and C(8)

$0.7771x + 0.1952y + 0.5983z = 6.9700$

C(14) =	−0.1141	C(16) =	−0.1416

(f) Plane based on C(6), C(7), C(8) and N(1)

$0.2805x + 0.7420y - 0.6089z = 3.2241$

C(6)	0.0588	C(8)	0.1181
C(7)	−0.0691	N(1)	−0.1073
Mo	−1.1131		

Angle between planes

Plan 1	Plan 2	Angle
(d)	(b)	77.70
(d)	(e)	57.31
(b)	(e)	45.37
(a)	(f)	5.94

TABLE VIIb. Least Squares Planes (in Orthogonal Å Space) and Deviation of Atoms from these Planes (in Å) for Crystal II.

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

$0.4024x + 0.3162y + 0.8591z = 1.7746$

C(1)	−0.0088	C(2)	0.0028
C(3)	0.0047	C(4)	−0.0099
C(5)	0.0112	Mo	2.0323

(b) Plane based on C(9), C(10), C(11), C(12), C(13), and N(2)

$0.8356x + 0.3786y + 0.3980z = 4.3392$

C(9)	−0.0050	C(10)	−0.0018
C(11)	0.0088	C(12)	−0.0097
C(13)	0.0034	N(2)	0.0043
C(8)	−0.0680	N(1)	−0.4574

(c) Plane based on C(17), C(18), C(19), C(20), C(21), and C(22)

$-0.5994x + 0.6937y - 0.3994z = -1.6668$

C(17)	0.0172	C(18)	−0.0236
C(19)	0.0104	C(20)	0.0089
C(21)	−0.0151	C(22)	0.0023

(d) Plane based on Mo, N(1) and C(8)

$-0.2534x + 0.1313y + 0.9584z = 3.9327$

(e) Plane based on C(8), N(1), and C(14)

$0.9297x - 0.0050y - 0.3684z = 0.3491$

C(17)	−0.0997	C(15)	−0.2393

(f) Plane based on C(6), C(7), C(8) and N(1)

$0.2625x + 0.2970y + 0.9181z = 5.0751$

C(6)	0.0590	C(8)	0.1033
C(7)	−0.0607	N(1)	−0.1017
Mo	−1.0707		

Angle between planes

Plan 1	Plan 2	Angle
(d)	(b)	77.33
(d)	(e)	53.89
(b)	(e)	57.07
(a)	(f)	8.77

complexes listed. Thus, the Mo atom is closer to the Cp ring in compounds (III) and (IV) than in (I) and (II) and this seems to be accompanied by a parallel increase in the Mo–C(O) distances. The variations in the CO distances are small and of doubtful significance. As previously stated, the Mo–N distances found in compounds (I) and (II) are significantly shorter than the Mo–C bonds. However, this has no effect on the *trans* carbonyl carbons, both whose Mo–C distances are identical within 1σ. The Mo–N distances remain virtually constant for all the compounds listed in Table IX.

TABLE VIII. Determination of the Absolute Configuration of Compound (II).

Reflection Number	Indices	F(calc.) hkl	F(calc.) $(\bar{h}\bar{k}\bar{l})$	Calc. F[a] ratio	Meas. F[b] ratio
1	1, 3, 12	33.84	35.93	0.94	0.96
2	1, 1, 7	21.25	19.57	1.09	1.08
3	2, 2, 2	77.22	80.00	0.97	0.98
4	2, 2, 3	57.55	55.26	1.04	1.04
5	2, 2, 4	31.47	28.82	1.09	1.10
6	2, 4, 3	100.85	104.07	0.97	0.97
7	2, 6, 1	42.50	44.81	0.95	0.96
8	3, 5, 4	8.87	7.65	1.16	1.12
9	3, 3, 5	22.41	23.98	0.93	0.95

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

TABLE IX. A Comparison of Molecular Parameters of the (η^5-C_5H_5)Mo(CO)$_2$ Unit with some Literature Values (Distances in Å, angles in deg.).

Compound	Mo–(η^5-C_5H_5)	Mo–C(O)	C–O	Mo–N	(O)C–Mo–C(O)	Ref.
(I)	2.047	1.933(12) 1.932(13)	1.172(15) 1.157(16)	2.178(8)	78.4(6)	This work
(II)	2.032	1.932(8) 1.937(8)	1.180(10) 1.183(12)	2.177(6)	78.7(3)	This work
(III)	2.005	1.984(14) 1.988(14)	1.120(18) 1.136(17)	2.182(10)	73.5(6)	20
(IV)	1.992	1.938(4) 1.977(4)	1.169(4) 1.156(4)	2.220(3)	73.3(2)	21

The geometry of the various groups such as the Cp, -CH(CH_3)(C_6H_5), -CH(CH_3)$_2$, pyridine, phenyl and the carbonyl groups is normal.

The orientation of the pyridyl group is determined by the formation of a strong intramolecular interaction between its nitrogen and the N(1)–H(6) group. The relevant parameters found for compound (I) are; N(1)---N(2) = 2.61(1), N(2)---H(6) = 1.89(12) Å and angle N(1)–H(6)---N(2) = 115(6)°. For compound (II) (for which only the theoretical hydrogen positions were determined) an N(1)---N(2) separation of 2.66(1) Å was observed. The close N(2)---H(6) contact of 1.89(12) Å, which is much shorter than the sum of the van der Waals radii for these elements, and the fact that the N(1)–H(6) group is approximately coplanar with the pyridine ring (see Tables VIIa, b) seem to indicate that these interactions are formal hydrogen bonds. According to a recent survey by Whuler *et al.* [18], these interactions would be classified as strong N–H--N type hydrogen bonds. The angle at H(6) is quite small, however somewhat similar low values have been measured before [19].

Figures 2 and 5 give convenient stereoviews of molecules (I) and (II), respectively. The dominant structural feature of these compounds is the *trans* arrangement of the large alkyl or aryl substituent, R, and the pyridine ring with respect to the three membered ring plane. The different substituents at the C and N atoms of the three membered chelate ring have the same position relative to the (η^5-C_5H_5) ring in both derivatives.

Acknowledgements

We thank the U.S. National Science Foundation for providing funds for the purchase of the diffractometer and the Robert A. Welch Foundation for research grants. Finally, we are greatful to the Computer Center of the University of Houston for a generous supply of free computing time.

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