Structure of (η-Allyl)dicarbonyl(pentane-2,4-dionato)pyridinemolybdenum(II) in the Solid and Solution States

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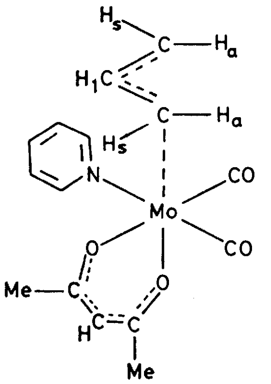
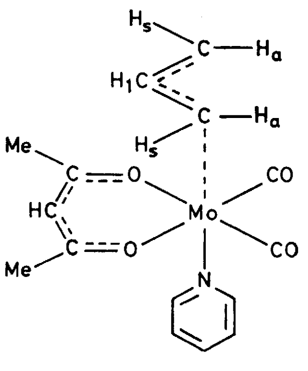
Crystals of the title complex are monoclinic, space group $P2_1/c$, with a = 6.945(1), b = 24.946(6), c = 9.389 (2) Å, β = 93.71(1)°, and Z = 4. The structure, solved by the heavy-atom method and refined to R 0.032 for 2 275 independent reflections, contains an Mo(allyl)(CO)$_2$ unit of approximate C_s symmetry. The molecule as a whole becomes asymmetric when the pseudo-octahedral co-ordination around molybdenum is completed with dionate oxygens and a nitrogen atom which is *trans* to one of the *cis*-dicarbonyl ligands. This configuration makes the allyl nuclei non-equivalent as observed in the ^{1}H and ^{13}C n.m.r. spectra at low temperatures. A symmetrical isomer is also detectable at low temperatures, whereas the molecule is fully fluxional at room temperature. The isomer ratio at a particular temperature is dependent on the nature of the solvent.

Two possible structures (A) and (B) were suggested for the complex [Mo(η-C$_3$H$_5$)(CO)$_2$(pd)(py)] (pd = pentane-2,4-dionate, py = pyridine). Structure (B) was considered the more likely in view of the simple AM$_2$X$_2$ allyl ^{1}H n.m.r. spectrum observed at room temperature,[1] and the known crystal structures of similar (η-allyl)dicarbonylmolybdenum complexes.[2-4] However, variable-temperature ^{1}H n.m.r. investigations in CDCl$_3$ yielded results incompatible with a single structure (A) or (B), and in order to resolve this apparent anomaly an X-ray determination of the solid structure was undertaken in conjunction with ^{13}C n.m.r. studies on solutions of the complex.



(A)



(B)

EXPERIMENTAL

The complex [Mo(η-C$_3$H$_5$)(CO)$_2$(pd)(py)] was prepared as reported previously[1] and recrystallised from aqueous pyridine under an atmosphere of nitrogen. One of the elongated prisms, cut to dimensions 0.4 × 0.2 × 0.25 mm, was sealed in a Lindemann capillary. Intensity data were collected at ambient temperatures on a Syntex $P2_1$ four-circle diffractometer over the 2θ range of 3.3—50.0° using Mo-K_α radiation as described previously.[5] Of 3 132 measured intensities, 2 275 unique reflections for which $I > 2.5\sigma(I)$ were used to solve the structure. Corrections were applied for Lorentz and polarisation effects but not for absorption.

Crystal Data.—C$_{15}$H$_{17}$MoNO$_4$, M = 371, Monoclinic, a = 6.945(1), b = 24.946(6), c = 9.389(2) Å, β = 93.71(1)°, U = 1 623.5(6) Å^3, D_m (flotation) = 1.48 g cm^{-3}, Z = 4, D_c = 1.52 g cm^{-3}, $F(000)$ = 752, Mo-K_α X-radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 8 cm^{-1}, space group $P2_1/c$ (no. 14).

Structure Solution and Refinement.—The molybdenum atom was located from a Patterson synthesis, and the positions of other non-hydrogen atoms by subsequent electron-density difference syntheses. Refinement proceeded with sufficient atoms allowed anisotropic thermal movement until all the hydrogen atoms showed up clearly in a difference synthesis. The remaining non-hydrogen atoms were made anisotropic at this stage using two block matrices. The allocation of atom parameters between the matrices was not critical. In the final refinement a simple scheme gave low weighting to reflections having high F_o or low sin θ values [unit weights for sin $\theta > 0.28$ or $F_o > 45$; other weights taken as (sin θ)/0.28 or $45/F_o$]. The residual index converged to R 0.032 (R' 0.036) with an average shift-to-error ratio of 0.005 4. No peaks of >0.2 or < −0.2 eÅ^{-3} appeared on the final difference map. The 'X-Ray' system of programs[6] was used for computation after the initial data reduction. Observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 22190 (15 pp.).†

N.M.R. Spectra.—Hydrogen-1 n.m.r. spectra were recorded on a JEOL PS100 spectrometer equipped with a variable-temperature attachment (VT-38). A JEOL PFT-100 spectrometer operating in the Fourier-transform mode at 25.15 MHz was used to obtain ^{13}C n.m.r. spectra.

RESULTS AND DISCUSSION

Solid-state Structure.—The structure and atom numbering of a single molecule is shown as a projection on the *ac* plane in Figure 1, and the packing of molecules within the unit cell projected on the *bc* plane is shown in Figure 2. Atomic positional parameters and significant interatomic distances and bond angles are in Tables 1 and 2.

The ligand arrangement is essentially that in structure (A) and unlike that in other known structures of [Mo(η-C$_3$H$_5$)(CO)$_2$(bidentate)L] species (L = a two-electron unidentate ligand) which adopt the more

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

[1] B. J. Brisdon and G. F. Griffin, *J.C.S. Dalton*, 1975, 1999.

[2] A. J. Graham and R. H. Fenn, *J. Organometallic Chem.*, 1969, **17**, 405; 1970, **25**, 173; 1972, **37**, 137.

[3] F. A. Cotton, B. A. Frenz, and A. G. Stanislowski, *Inorg. Chim. Acta*, 1973, **7**, 503.

[4] F. Dewans, J. Dewailly, J. Meuniert-Piret, and P. Piret, *J. Organometallic Chem.*, 1974, **76**, 53.

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[6] Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

TABLE 1

Atomic positional parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Mo	0.192 50(6)	0.112 36(2)	0.178 43(4)
Carbonyl groups			
C(1)	0.016 3(8)	0.053 2(2)	0.208 8(5)
O(1)	−0.091 7(7)	0.018 5(2)	0.226 9(5)
C(2)	−0.026 3(9)	0.133 7(2)	0.049 4(6)
O(2)	−0.160 2(7)	0.143 2(2)	−0.025 8(5)
Pentane-2,4-dionate ligand			
C(11)	0.570 3(15)	0.257 5(4)	0.235 0(10)
H(18) CH$_3$	0.550(9)	0.273(3)	0.154(7)
H(19) group	0.656(14)	0.241(4)	0.208(11)
H(20)	0.594(10)	0.277(3)	0.307(8)
C(12)	0.406 9(7)	0.219 7(2)	0.259 7(5)
O(3)	0.379 8(5)	0.182 0(1)	0.170 7(3)
C(13)	0.295 2(9)	0.227 7(2)	0.375 2(6)
H(13)	0.326(6)	0.248(2)	0.414(5)
C(14)	0.137 9(7)	0.198 7(2)	0.410 7(5)
O(4)	0.072 7(4)	0.156 8(1)	0.344 6(3)
C(15)	0.024 0(14)	0.216 1(4)	0.534 3(9)
H(15) CH$_3$	−0.092(9)	0.209(2)	0.522(6)
H(16) group	0.056(8)	0.244(2)	0.564(6)
H(17)	0.066(9)	0.197(2)	0.596(6)
Allyl ligand			
C(3)	0.271 3(12)	0.107 2(3)	0.055 8(6)
H(3)	0.315(10)	0.131(3)	−0.095(7)
H(33)	0.184(7)	0.085(2)	−0.117(6)
C(4)	0.396 5(9)	0.077 0(2)	0.034 9(6)
H(4)	0.528(9)	0.091(2)	0.058(6)
C(5)	0.314 9(10)	0.033 1(3)	0.095 3(7)
H(5)	0.391(7)	0.015(2)	0.145(5)
H(55)	0.217(8)	0.009(2)	0.044(6)
Pyridine ligand			
N	0.404 8(5)	0.092 1(2)	0.371 8(4)
C(6)	0.591 5(7)	0.103 9(2)	0.379 2(6)
H(6)	0.639(6)	0.117(2)	0.305(4)
C(7)	0.713 6(8)	0.095 7(2)	0.499 0(6)
H(7)	0.848(8)	0.103(2)	0.492(5)
C(8)	0.635 4(10)	0.075 1(3)	0.618 1(7)
H(8)	0.693(7)	0.073(2)	0.685(5)
C(9)	0.444 6(9)	0.061 9(2)	0.613 3(6)
H(9)	0.401(6)	0.047(2)	0.682(5)
C(10)	0.335 2(8)	0.070 5(2)	0.490 3(5)
H(10)	0.214(7)	0.058(2)	0.485(5)

symmetric type (B) structure.[2-4] Only the bis(pyrazolyl)borato-complexes [Mo(η-C_3H_5)(CO)$_2${BH$_2$(Me$_2$pz)$_2$}], [Mo(η-PhC_3H_4)(CO)$_2${BEt$_2$(pz)$_2$}], [Mo(η^3-C_7H_7)(CO)$_2${BH$_2$(pz)$_2$}], and [Mo(η-C_4H_7)(CO)$_2${BPh$_2$(pz)$_2$}] have related structures in which the bidentate pyrazolylborate ligand occupies co-ordination sites *trans* to one carbonyl group and the allyl ligand. However, the sixth co-ordination site is completed by C(B)–H–Mo bridges or remains vacant in these complexes.[7-10,*]

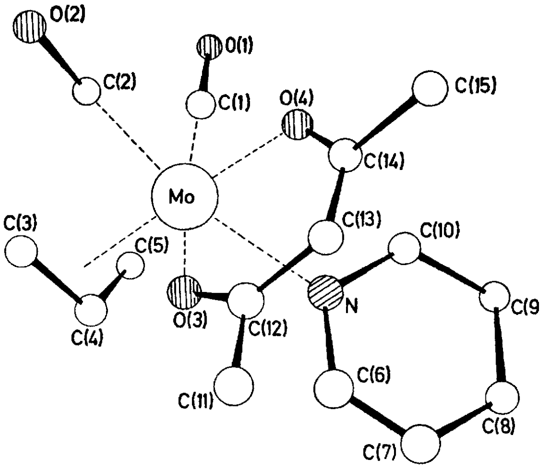

FIGURE 1 Projection of the molecule on the *ac* plane

The *fac*-Mo(η-C_3H_5)(CO)$_2$ moiety[†] occurs in all (η-allyl)-

TABLE 2

Interatomic distances (Å) and angles (°) with their standard deviations in parentheses

Allyl ligand			
C(3)–C(4)	1.397(9)	C(3)–C(4)–C(5)	115.1(6)
C(4)–C(5)	1.371(9)	Σ C(3) * 344(14), ΣC(5) 347(12),	
C(3)–C(5)	2.336(10)	Σ C(4) 360(8)	
Mean C–H 0.91(6)			
Carbonyl ligands			
C(1)–O(1)	1.165(8)	C(1)–Mo–C(2)	79.9(2)
C(2)–O(2)	1.153(8)	Mo–C(1)–O(1)	179.4(5)
		Mo–C(2)–O(2)	175.8(6)
Pyridine ligand			
N–C(6)	1.327(6)	N–C(6)–C(7)	123.8(5)
C(6)–C(7)	1.380(6)	C(6)–C(7)–C(8)	117.7(5)
C(7)–C(8)	1.373(9)	C(7)–C(8)–C(9)	119.9(6)
C(8)–C(9)	1.364(9)	C(8)–C(9)–C(10)	118.6(5)
C(9)–C(10)	1.358(7)	C(9)–C(10)–N	123.5(5)
C(10)–N	1.353(6)	C(10)–N–C(6)	116.4(4)
Mean C–H	0.86(5)	Mo–N–C(10)	119.2(3)
Mo–N	2.319(4)	Mo–N–C(6)	124.2(3)
		O(4)–Mo–N	78.3(1)
		O(3)–Mo–N	81.3(1)
Pentane-2,4-dionate ligand			
C(11)–C(12)	1.503(11)	C(11)–C(12)–O(3)	116.4(5)
C(12)–O(3)	1.263(6)	C(11)–C(12)–C(13)	119.7(6)
C(12)–C(13)	1.388(8)	O(3)–C(12)–C(13)	123.8(5)
C(13)–C(14)	1.369(8)	C(12)–C(13)–C(14)	127.6(5)
C(14)–O(4)	1.283(6)	O(4)–C(14)–C(13)	125.1(5)
C(14)–C(15)	1.510(11)	C(13)–C(14)–C(15)	120.0(6)
Mean C–H	0.80(7)	C(15)–C(14)–O(4)	114.9(5)
Mo–O(3)	2.174(3)	O(4)–Mo–C(1)	90.4(2)
Mo–O(4)	2.126(3)	O(4)–Mo–C(2)	89.1(2)
		O(3)–Mo–C(1)	172.8(2)
Others			
Mo–C(1)	1.949(5)	C(2)–Mo–N	166.7(2)
Mo–C(2)	1.958(6)	C(2)–Mo–C(4)	103.5(2)
Mo–C(3)	2.304(6)	C(4)–C(3)–Mo	68.2(4)
Mo–C(4)	2.202(6)	C(4)–C(5)–Mo	68.0(3)
Mo–C(5)	2.306(7)	C(1)–C(5)–C(3)	91.3(3)
C(1)–C(5)	2.449(9)	C(2)–C(3)–C(5)	92.6(3)
C(2)–C(3)	2.451(10)	C(4)–Mo–N	89.5(2)

* Σ C(n) is the sum of angles around this central atom, together with the summed standard deviations in parentheses.

[*] A recent preliminary communication (J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, *J. Amer. Chem. Soc.*, 1977, **99**, 1654) indicates that [MoCl(η-C_3H_5)(CO)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] also has the unsymmetrical structure (A) although no interatomic distances or bond angles have yet been published.

[†] Although these complexes are *formally* seven-co-ordinate with the η-allyl group bidentate, all the three carbon atoms are involved in some degree of metal–η-allyl bonding so that from a structural point of view these complexes are considered to be pseudo-octahedral with only one metal–allyl linkage.

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[7] F. A. Cotton, T. La Coeur, and A. G. Stanislowski, *J. Amer. Chem. Soc.*, 1974, **96**, 754.

[8] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **42**, 419.

[9] F. A. Cotton, B. A. Frenz, and C. A. Murillo, *J. Amer. Chem. Soc.*, 1975, **97**, 2118.

[10] C. A. Kosky, P. Ganis, and G. Avitabile, *Acta Cryst.*, 1971, **B27**, 1859.

dicarbonylmolybdenum(II) complexes so far investigated and must be related to the relatively high stability shown by these complexes compared with other molybdenum(II) derivatives. In [Mo(η-C_3H_5)$(CO)_2$(pd)(py)], the geometry of this unit is readily appreciated by consideration of the approximately rectangular plane defined by C(3)–C(5)–C(1)–C(2). The allyl group and the carbonyl groups are in an *anti*-configuration with respect to this plane whilst the vertical plane present in the allyl group is retained in the larger unit (Figures 3 and 4). The molybdenum atom is on this vertical plane, which also bifurcates the carbonyl groups, and is almost equidistant from the carbonyl carbons (1.955 ± 0.005 Å) and the plane through the three allyl carbon atoms (the *perpendicular* distance from Mo to the allyl plane is 1.974 Å). The dionate oxygen O(4) is symmetrically placed with respect to the allyl group and the carbonyls [*i.e.* perpendicular to the C(2)–Mo–C(1) plane], and it is only when the dionate oxygen O(3) and the pyridine nitrogen (N) are considered that the unit as a whole becomes asymmetric. These last two ligands would cause each nucleus in the allyl group to give a distinctive n.m.r. signal if the same geometry were retained in solution. Interchanging O(3) and the pyridine ligand results in structure (B) in which the terminal allyl carbon atoms and pairs of *syn*- and *anti*-allyl protons should show equivalence.

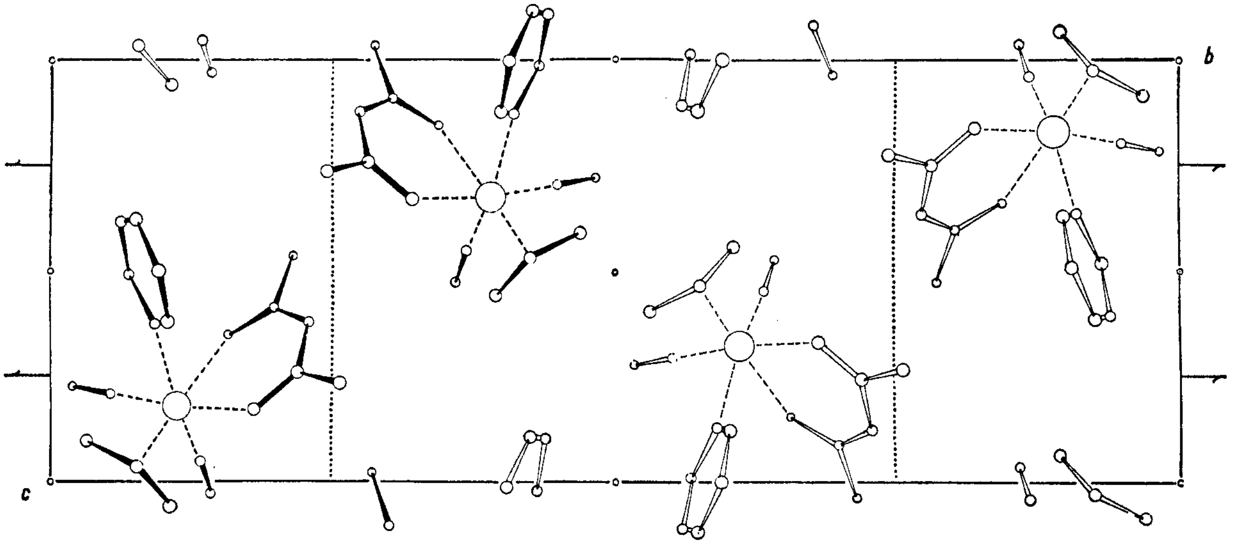


FIGURE 2 Packing of molecules in the unit cell projected on the *bc* plane

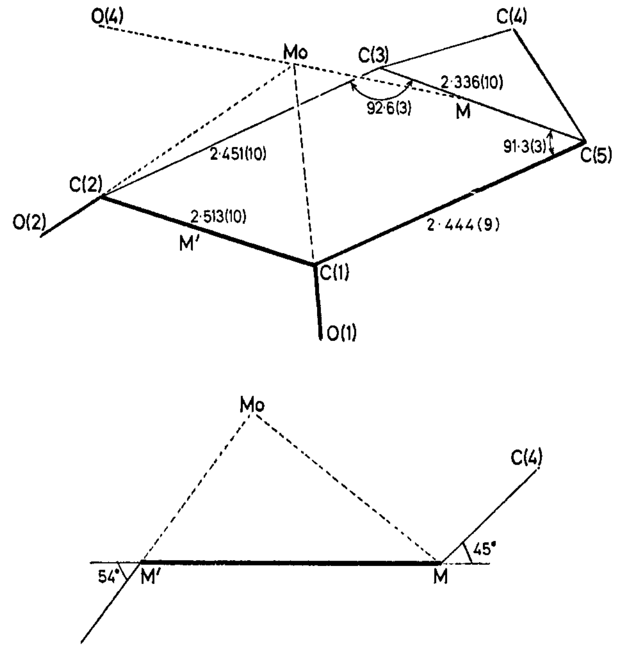


FIGURE 3 View of the Mo(η-C_3H_3)$(CO)_2$ unit with median section [M'–Mo–M–C(4)]

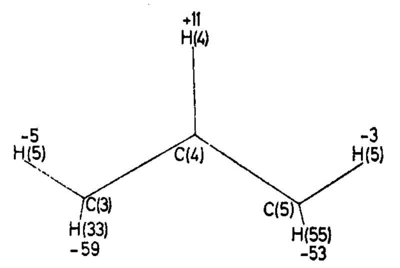
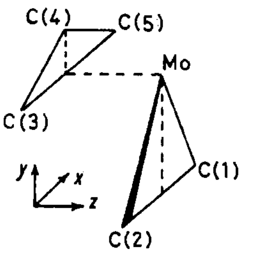


FIGURE 4 The allyl group viewed perpendicular to the C(3)–C(4)–C(5) plane with distances from this plane in pm (Mo is above the plane)



The constancy of the Mo(η-allyl)$(CO)_2$ unit in the solid structures so far examined is summarised in Table 3. The apparent exception is a tetrafluoroborate salt. The unit within the cation has a more asymmetric allyl group and more distant carbonyl groups than in neutral complexes. For neutral complexes the geometry of this unit is little affected by the type or position of other ligands.

TABLE 3

Geometry of the Mo(η-allyl)$(CO)_2$ unit in different structures

		Allyl geometry [b]			Molybdenum distances (Å)					
		Interatomic distances (Å)		Bond angles (°)				Mean (Å) of Mo–C(1) and Mo–C(2)	Angle (°)	
R index	Ligands [a]	C(4)–C(5)	C(4)–C(3)	C(3)–C(4)–C(5)	C(4)	C(3)	C(5)		C(1)–Mo–C(2)	Ref.
0.086	bipy,*N*CS [c]	1.46	1.42	116	2.20	2.29	2.35	1.93	78.3	2
0.082	bipy,py	1.47	1.37	111	2.28	2.29	2.31	1.99	78.2	2
0.027	$BEt_2(pz)_2$, pz	1.41	1.39	117	2.21	2.34	2.35	1.95	81.4	3
0.118	dme, *O*OCCF$_3$	1.45		114	2.16	2.34	2.34	1.90	79	4
0.054	BH*H*$(Me_2pz)_2$	1.42	1.35	118	2.21	2.33	2.36	1.95	79.8	10
0.030	$BPh(pz)_3$	1.42	1.42	116	2.22	2.34	2.37	1.92	79.1	*d*
0.032	pd, py	1.40	1.37	115	2.20	2.30	2.31	1.95	79.9	This work

[a] bipy = 2,2′-Bipyridine; dme = 1,2-dimethoxyethane. [b] Carbon atoms numbered as in Figure 1. [c] The ligand atom is italicised when required for clarity. [d] F. A. Cotton, C. A. Murillo, and B. R. Stults, *Inorg. Chim. Acta*, 1977, **22**, 75.

The nature of metal–η-allyl bonding has been discussed previously.[11–13] From the tilt angles observed it seems that the major overlaps are $\psi_2 - d_{xz} - \pi_g$, where ψ_2 is the molecular orbital (m.o.) formed from the terminal allyl carbons and π_g is the lowest unoccupied m.o. on CO, and a contribution $\psi_1 - d_{z^2} - \sigma_g$ where all the allyl carbon atoms contribute to ψ_1 and back donation is possible from the highest occupied m.o. (σ_g) on CO.

TABLE 4

Hydrogen-1 n.m.r. data (δ/p.p.m.) * at 210 K for $[Mo(\eta\text{-}C_3H_5)(CO)_2(pd)(py)]$

In $CDCl_3$	In $(CD_3)_2CO$	Assignment and relative intensity
1.23(d)	1.16(d)	H_a(A)
	1.52(d)	H_a(A)
1.56(dd)		H_a(A) + 2 H_a(B)
	1.80(s)	3 H(pd)(A)
1.81(s)		3 H(pd)(A), 6 H(pd)(B)
1.89(s)		3 H(pd)(A)
	1.94(s)	3 H(pd)(A)
2.78(d)	2.78(d)	H_s(A)
3.44(m)		H_s(A), 2H_s(B), H_1(B), H_1(A)
	3.60(m)	H_s(A), H_1(A)
5.00(s)	5.19(s)	CH(pd)(A)
5.04(s)		CH(pd)(B)
7.19(m)	7.51(t)	H_o(py)(A)
7.35(m)		H_o(py)(B)
7.66(m)	7.98(t)	H_m(py)(A)
7.70(m)		H_m(py)(B)
8.12(d)	8.35(d)	H_p(py)(A)
8.48(d)		H_p(py)(B)

* Relative to $SiMe_4$; d = doublet, dd = doublet of doublets, s = singlet, t = triplet, and m = multiplet.

N.M.R. Data.—At room temperature and above the ^1H n.m.r. spectrum of the complex is at variance with the structure established for the solid. An AM_2X_2 pattern is observed for the allyl protons, and a single resonance for the methyl protons of the pentanedionate group.[1] However, on cooling $(CD_3)_2CO$ solutions of the complex the proton signals initially broaden and below 270 K the *syn*- and *anti*-proton signals and the pentanedionate methyl resonance each begin to separate into two components. Below 230 K, ^1H and ^{13}C n.m.r. data are in accord with the solid-state geometry (Tables 4 and 5).

In contradistinction, the low-temperature ^1H and ^{13}C n.m.r. spectra in $CDCl_3$ indicate the presence of a second isomer. Neither the *syn*- nor the *anti*-proton signals of this second isomer are split and the ^{13}C n.m.r. data (Table 4) indicate that both the carbonyl ligands, and the CO groups of the β-diketonate ligand, are equivalent in pairs. This is consistent with a structure containing a plane of symmetry such as (B). An isomer ratio (A : B) of *ca.* 1.6 : 1 at 210 K in $CDCl_3$ was derived from intensity measurements. On repeating the measurements at 210 K in $(CD_3)_2CO$ and using very concentrated solutions, trace amounts of the symmetric isomer (<10%) were also detected in this solvent.

TABLE 5

Carbon-13 n.m.r. data (δ/p.p.m.) * at 210 K for $[Mo(\eta\text{-}C_3H_5)(CO)_2(pd)(py)]$

In $CDCl_3$	In $(CD_3)_2CO$	Assignment and relative intensity
228.19	229.22	CO(A)
228.16(sh)	229.19	CO(A)
227.94		2CO(B)
189.05	190.02	CO(pd)(A)
188.75		2CO(pd)(B)
185.96	186.69	CO(pd)(A)
150.65		C_o(py)(B)
150.29	151.26	C_o(py)(A)
138.20		C_p(py)(B)
137.67	138.94	C_p(py)(A)
124.74		C_m(py)(B)
124.38	125.47	C_m(py)(A)
100.16(sh)		CH_1(B)
100.11	100.47	CH_1(A)
72.26	72.93	CH(pd)(A)
71.17		CH(pd)(B)
61.16		$2CH_2$(allyl)(B)
60.55	60.55	CH_2(allyl)(A)
57.27	57.03	CH_2(allyl)(A)
28.21	28.39	CH_3(pd)(A), $2CH_3$(pd)(B)
	28.03	CH_3(pd)(A)
27.61	27.36	CH_3(pd)(A)

* At 295 K the terminal allyl carbon and dionate methyl resonances appeared as single bands [δ 59.10 and 27.60 p.p.m. respectively in $(CD_3)_2CO$] in the ^{13}C n.m.r. spectrum of the complex.

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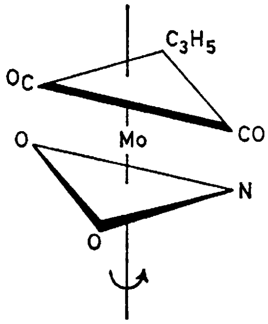
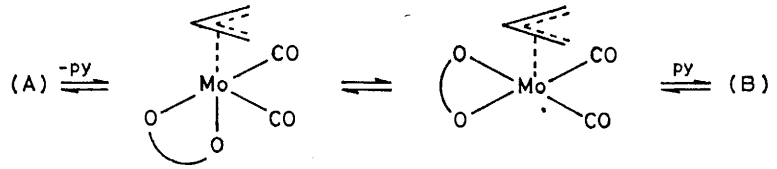
[12] P. W. N. M. Van Leeuwen and A. P. Praat, *J. Organometallic Chem.*, 1970, **21**, 501.

[13] H. L. Clarke, *J. Organometallic Chem.*, 1974, **80**, 155.



(1)

Both the stereochemical non-rigidity of the complex at room temperature and the existence of isomeric species at lower temperatures can be explained by alternative mechanisms. In (1), rotation of one half of the molecule with respect to the $Mo(\eta\text{-}C_3H_5)(CO)_2$ unit occurs, as found in the complex $[Mo(\eta\text{-}C_3H_5)(CO)_2\text{-}\{BR(pz)\}]$.[14] In (2), the complex having structure (A) first loses pyridine, then rearranges to a square-pyramidal intermediate, and pyridine is added *trans* to the allyl group. The latter scheme is less likely because, up to room temperature, free and ligated pyridine exhibit separate and well resolved n.m.r. signals. Temperatures above 320 K are required for fast exchange of this ligand. Mechanism (1) is compatible with the bond lengths obtained in the solid, which show that the $Mo(\eta\text{-}C_3H_5)(CO)_2$ moiety is a tightly bound unit whereas the other facial set of ligands is further removed from the central metal atom by 0.24 Å on average.



(2)

An approximate activation energy of 60 kJ mol^{-1} was calculated from the temperature dependence of the ^{1}H n.m.r. spectrum in $(CD_3)_2CO$. This compares favourably with values found for the similar rotation process in pyrazolylborato-complexes of Mo^{II},[14,15] and further emphasizes the similarities in ligand properties noted for some pyrazolylborate and β-diketonate anions.[14]

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