ORGANOMETALLIC CONFORMATIONAL EQUILIBRIA

XVI*. STERIC EFFECTS ON π-ALLYL AND π-INDENYL ORIENTATION IN MOLYBDENUM AND TUNGSTEN COMPLEXES

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(Received August 4th, 1972)

SUMMARY

Steric effects on π-allyl and π-indenyl orientation in molybdenum and tungsten complexes have been studied. Magnetic anisotropies associated with indenyl derivatives have provided a definitive technique for determination of stereochemistry in these complexes. The steric factors which determine the stability of the orientations of the allyl moiety have been discussed. Generally π-cyclopentadienyl or π-indenyl ligands have been considered to be essentially freely rotating. Analysis of the magnitude of the magnetic anisotropy arising from the benzene ring has suggested that there is relatively free rotation of the indenyl ligands, but there is a preferred conformation with the six-membered ring oriented over the allyl. Appropriate substitution on the allyl offers sufficient steric hindrance to make other conformations more probable.

INTRODUCTION

The possibility of different modes of bonding of the allyl moiety in π-cyclopentadienyl-π-allylmolybdenum dicarbonyl was originally noted by King[1]. Davison and Rode[2] demonstrated that a rapid conformational equilibrium did indeed exist in this compound and our subsequent work[3] suggested assignments of the two configurations on the basis of steric arguments. Conformational equilibria between conformers of π-allyl derivatives of molybdenum and tungsten complexes have been widely noted[4–7]; nevertheless, convincing evidence for assigning given configurations was lacking until the large magnetic anisotropies associated with indenyl derivatives provided a definitive technique for the determination of stereochemistry[8]. We have surveyed a series of substituted allyl complexes to assess the importance of steric factors in determining the orientation of the allyl moiety. Interactions determining conformational preferences of the π-indenyl ligand have also been considered.

RESULTS AND DISCUSSION

Criteria for isomer assignment

The presence of four carbonyl stretching bands in the IR spectrum of π-C_5H_5-

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* For Part XV see ref. 36.
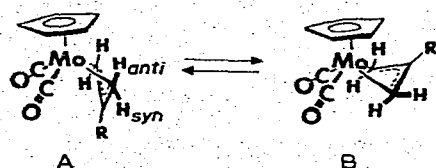
Fig. 1. The two stable configurations of the allyl moiety.

π-$C_3H_5Mo(CO)_2$ originally suggested the existence of two distinct structures in solution[1]. Subsequently, both IR and temperature dependent NMR spectra have been rationalized in terms of equilibria involving conformation A and B[2,3]. The choice of these particular structures is based upon a wealth of crystallographic data on compounds having the general formula, π-$C_5H_5Mo(CO)_2LR$[9-13]. These complexes may be formally regarded as seven-coordinate complexes of molybdenum with the cyclopentadienyl ring occupying three coordination positions. The remaining ligands are located approximately at the corners of a square in an idealized configuration similar to a square pyramid. Replacing the *cis* ligands by a chelating π-allyl suggests the possibility of the two configurations differing principally in the orientation of the allyl moiety. The recent X-ray structural analysis of π-benzyl-π-cyclopentadienyl-molybdenum dicarbonyl, which contains a π-allyl–Mo linkage, further substantiates this suggested geometry[14].

For a series of substituted π-allyl moieties, both IR and NMR spectra confirmed the presence of two isomers in solution. Although the substitutions caused drastic changes in relative concentrations of isomers, correlations were found between the frequencies of the IR bands and the chemical shifts throughout the series.

These correlations are attributed to one isomer generally giving rise to resonances for the *anti* protons approximately 0.6 to 1.0 ppm to higher field of the others,

TABLE 1

NMR AND IR DATA FOR π-CYCLOPENTADIENYL AND
π-INDENYL-π-ALLYLMOLYBDENUM DICARBONYL

	Major		Minor	
	C_5H_5	C_9H_7	C_5H_5	C_9H_7
ν_s(CO) (cyclohexane)[a]	1963	1963	1970	1971
ν_a(CO) (cyclohexane)[a]	1889	1887	1903	1902
δ anti protons[b]	1.02	1.15	1.64	-0.68
δ syn protons[b]	2.70	2.39	2.77	3.60
δ central proton[b]	3.61	0.15	3.61	3.37
J(central–syn)[c]	7.30	7.50	6.40	6.70
J(central–anti)[c]	10.80	11.40	10.50	10.70
J(anti–syn)[c]	2.20	2.20	< 0.60	< 0.70
δ terminal carbons[d]	152.76	144.13	156.21	137.99
δ central carbon	125.25	[e]	106.80	[e]
δ C_5H_5[d]	101.19	[e]	102.38	[e]

[a] cm^{-1}. [b] ^{1}H resonance in ppm downfield from TMS in benzene solution. [c] Absolute value of ^{1}H–^{1}H coupling in Hz. [d] ^{13}C resonance in ppm upfield from CS_2 in 85/15 CS_2/C_6F_6 at 7°. [e] Overlap of resonances has presented difficulties in providing reliable assignments.

as well as carbonyl stretching frequencies ≈ 10 cm^{-1} lower than the other. A consistent interpretation and assignment throughout the series is possible on the basis of steric factors; however, for clarity the structural elucidation of the parent allyl complex will be considered separately and then extended to the homologs.

Comparison of the intensities of IR carbonyl stretching frequencies and relative areas of proton resonances has demonstrated that substitution of an indenyl ligand for a cyclopentadienyl ligand does not greatly alter the ratio of allyl conformers, although the barrier to interconversion of the conformers is raised somewhat. Comparison of the proton chemical shifts, however, shows large differences attributable to the magnetic anisotropy of the indenyl ring. In comparing the allyl resonances of the indenyl complex with those of the cyclopentadienyl complex, an upfield shift is expected for the protons which approach nearest the benzene ring, i.e., the anti protons of the allyl in A and the central proton in B. Thus the upfield shift ($\delta_{anis} + 1.32$) of the anti resonances of the minor isomer of the allyl establish it as A; whereas the upfield shift ($\delta_{anis} + 3.46$) of the central proton of the major isomer establish it as B. Reference to Table 1 illustrates the similarities between the cyclopentadienyl and indenyl analogs and points out the characteristics of each isomer.
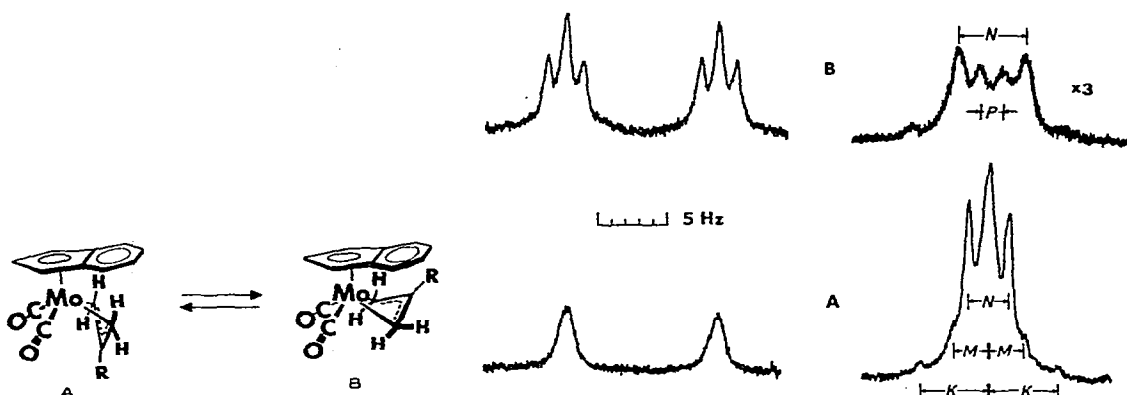

Fig. 2. Orientations of the indenyl ligand which give rise to large magnetic anisotropies for allyl protons.

Fig. 3. Proton magnetic resonance spectra of the *anti* protons in the AA'BB'-type spectra of π-cyclopentadienyl-π-allylmolybdenum dicarbonyl on the left and π-cyclopentadienyl-π-(2-chloroallylmolybdenum dicarbonyl) on the right. The spectra were taken in carbon disulfide at −15°. The standard terminology for the observed splittings is indicated except for *P*. The usual value, *L*, is determined from the observed value of *K*, and $P = -K + (K^2 + L^2)^{\frac{1}{2}}$.

Throughout the series of substituted derivatives, the most reliable characteristics for B appear to be: the ≈ 10 cm^{-1} lower carbonyl stretching frequencies; the ≈ 0.6 ppm higher field shift of the anti protons in the cyclopentadienyl derivatives; the large δ_{anis} for the central proton*; and the larger coupling between the syn and anti protons (≈ 2 Hz in alkyl substituted allyls).

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* A less reliable but fairly characteristic property of the isomers is an upfield shift of the syn protons in the B configuration ($\delta_{anis} \approx +0.3$ ppm) and a downfield shift in the A configuration ($\delta_{anis} \approx -0.9$ ppm).

TABLE 2

CHEMICAL SHIFTS FOR THE COMPOUNDS π-CYCLOPENTADIENYL- AND π-INDENYL-π-ALLYLMETAL DICARBONYL

M π-Allyl	Major isomer	Assignment	Chemical shift[a]			
			π-C_5H_5		π-Indenyl	
			Major	Minor	Major	Minor
Mo	B	π-C_5H_5[b]	5.10	5.10	5.84	5.83
(in $CDCl_3$)					5.51	5.46
		c-H	3.92	3.58	0.12	3.37
		s-H	2.78	2.72	2.32	3.46
		a-H	0.88	1.76	0.97	−0.78
Mo 2-Cl	A	π-C_5H_5[b]	5.18	5.29	6.19	
(in $CDCl_3$)					5.71	
		s-H	3.16	3.26	4.02	
		a-H	2.31	1.37	−0.39	
Mo 2-Br	A	π-C_5H_5[b]	5.14	5.31	5.91	
(in $CDCl_3$)					5.45	
		s-H	3.12	3.19	3.79	
		a-H	2.35	1.44	−0.25	
Mo 2-Me	A	π-C_5H_5[b]	5.16	5.14	5.87	
(in $CDCl_3$)					5.43	
		c-CH_3	1.70	1.75	1.49	
		s-H	2.76	2.83	3.46	
		a-H	1.92	0.94	−0.72	
Mo 1-Me	B	π-C_5H_5[b]	5.17	5.12	5.95[c]	5.95[c]
(in CS_2)					5.73	5.73[c]
					5.59	5.47
		c-H	3.90	3.50	0.52	3.16
		s'-CH_3	1.84	1.98	1.63	1.94
		s-H	2.53	2.60	1.88	3.27
		a'-H	1.67	2.76	1.55	−0.16
		a-H	0.72	1.60	0.82	−0.67
Mo 1,1-Me_2	B	π-C_5H_5[b]	5.14		5.91[c]	
(in $CDCl_3$)					5.69[c]	
					5.53	
		c-H	3.99		−0.05	
		s'-CH_3	1.78		1.50	
		s-H	2.54		1.72	
		a'-CH_3	0.97		0.69	
		a-H	1.12		1.17	
Mo 1,3-Me_2	B	π-C_5H_5	5.23	5.14		
(in $CDCl_3$)		c-H	3.98	3.42		
		s-CH_3	1.69	1.85		
		a-H	1.39	2.60		
Mo 1,1,2-Me_3	B	π-C_5H_5[b]	5.12	5.12	5.25[c]	
(in CS_2)					5.37[c]	
					5.74	

(Continued)

TABLE 2   (continued)

| M π-Allyl	Major isomer	Assignment	Chemical shift[a]			
			π-C₅H₅		π-Indenyl	
			Major	Minor	Major	Minor
		c-CH₃	1.90	2.04	1.06	
		s'-CH₃	2.12	2.27	2.08	
		s-H	2.62	2.90	2.16	
		a'-CH₃	1.10	1.38	0.65	
		a-H	1.28	2.42	0.99	
W (in CDCl₃)	B	π-C₅H₅	5.25	5.22		
		c-H	3.54	3.67		
		s-H	2.73	2.70		
		a-H	1.07	1.64		
W 2-Me (in CDCl₃)	A	π-C₅H₅	5.17			
		c-CH₃	2.28			
		s-H	2.81			
		a-H	1.39			

[a] All measurements were performed at 100 MHz using 5% benzene as the field-resonance lock. Chemical shifts are in ppm downfield from tetramethylsilane; negative values imply resonances to higher field than TMS. [b] The assignment refers to the 1,3-H and 2-H in the indenyl group. The values in the first row are assigned to 1,3-H; those in the second row to 2-H. [c] The 1- and 3-H in the indenyl group become non equivalent when the allyl group is asymmetric. The specific assignments to 1-H or 3-H are unknown.

The greater *syn–anti* coupling in the B isomer is particularly striking in well-resolved spectra taken at low temperatures. The splittings observed must be interpreted in terms of coupling constants with care, since the resonances correspond to central lines of the A portion of an AA'BB'X spin system. Nevertheless, the larger splittings are readily observed and appear to be characteristic of the B isomer (see Fig. 3). In general, ^{13}C NMR shifts are susceptible to more subtle effects of conformation and do not provide reliable criteria for assigning isomer A or B.

Determination of major isomer configuration

The NMR data for the complexes prepared in this study are summarized in Tables 2–5. The major isomer of the 2-methyl, 2-chloro, and 2-bromo derivatives of the indenyl compound all show shifts for the *anti* protons above TMS, clearly indicating the predominance of the A configuration. In each of these cases a greater splitting of the *anti*-protons by *syn–anti* coupling is observed in the minor isomer. Comparison of IR spectra (Table 6) show that the high frequency components are more intense and therefore are assigned to the A configuration. The 1-methylallyl and 1,1-dimethylallyl derivatives of the cyclopentadienyl complex show an equilibrium similar to that of the unsubstituted allyl, the B configuration again predominating as indicated by the greater intensity of the low frequency carbonyl stretching modes or the higher field shifts of the *anti* proton of the major isomer. For the 1,1-dimethyl substituted derivative, the observation of only one central proton resonance 0.33 ppm below TMS in the indenyl complex clearly indicates the nearly exclusive presence of the B configuration. The coupling of 2.7 Hz between the *syn* and *anti* proton in this complex is

TABLE 3

COUPLING CONSTANTS FROM EXPERIMENTAL NMR SPECTRA OF ALLYLIC COMPOUNDS[a]
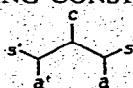
M	π-Allyl	Ring	Isomer	J(Ha–Hs)	J(Hc–Ha)	J(Hc–Hs)	J(Hc–Ra')	J(Ha–Ha')	J(Rs'–Ha')
Mo		Cp	A	[b]	10.5	6.4	10.5		
			B	[b]	10.8	7.3	10.8		
Mo		In	A	[b]	10.7	6.7	10.7		
			B	[b]	11.4	7.5	11.4		
W		Cp	A	[b]	9.5	5.6	9.5		
			B	[b]	10.4	6.9	10.4		
Mo	1-Me	Cp	A	<0.6	10.0	6.4	9.5	0	5.9
			B	2.4[c]	10.1	6.9	9.6	0	5.9
Mo	1-Me	In	A	<0.6	9[d]	7[d]	10[d]	0	5.5
			B	2.4[c]	10.0	7.1	9[d]	0	5.5
Mo	1,1-Me$_2$	Cp	A						
			B	3.1[c]	10.6	7.2	0.4[e]		
Mo	1,1-Me$_2$	In	A						
			B	2.7[c]	10.7	7.4	0.3[e]		
Mo	1,3-Me$_2$	Cp	A		9.6		9.6		5.7
			B		9.0		9.0		6.0
Mo	1,1,2-Me$_3$	Cp	A	<0.6					
			B	2.7					
Mo	1,1,2-Me$_3$	In	A						
			B	2.7					

[a] All coupling constants have errors smaller than ±0.2 Hz and are given as absolute values. Cp = π-cyclopentadienyl; In = π-indenyl. [b] See Table 5. [c] The sign of the coupling constant is negative as determined by spin tickling experiments and relationships to the positive signs of the coupling constants of the cis- and trans-vicinal protons, J(Hc–Ha) and J(Hc–Hs). [d] The error of these coupling constants is about ±0.5 Hz due to complicated spectra and second order coupling effects. [e] This is the coupling constant between the anti methyl group and the central proton.

TABLE 4

OBSERVED SPLITTINGS IN THE NMR SPECTRA OF 2-SUBSTITUTED-ALLYL COMPOUNDS

M	π-Allyl	Ring	Isomer	N	K	M	L
Mo		Cp	A	<0.6			
			B	2.4±0.1	3.1±0.5		
Mo		In	A	<0.7			
			B	2.2±0.1	3.2±0.5		
W		Cp	A	<0.6			
			B	2.8±0.1	3.3±0.5		
Mo	2-Br	Cp	A	3.3±0.1	4.9±0.2		1.6
			B	4.8±0.1	4.9±0.5		3.2
Mo	2-Br	In	A	3.2±0.1	4.8±0.3	2.6±0.3	1.4
			B				
Mo	2-Cl	Cp	A	2.9±0.1	4.8±0.2	2.6±0.3	1.4
			B	4.8±0.1	5.0±0.2	2.7±0.3	3.2
Mo	2-Me	Cp	A	<0.6			
			B	2.4±0.2			
Mo	2-Me	In	A	<0.6			

TABLE 5

THE CALCULATED COUPLING CONSTANTS FOR 2-SUBSTITUTED ALLYL COMPOUNDS[a]

M	π-Allyl	Ring	Isomer	$J_{ss'}$	J_{sa}	$J_{sa'}$	$J_{aa'}$
Mo		Cp	B	2.5	1.8	0.6	0.6
Mo		In	B	2.8	1.6	0.6	0.4
W		Cp	B	3.1	2.2	0.6	0.2
Mo	2-Br	Cp	B	3.5	4.2	0.6	1.4
			A	3.5	2.6	0.7	1.4
Mo	2-Br	In	B	3.4	2.6	0.6	1.4
Mo	2-Cl	Cp	B	3.6	4.2	0.6	1.4
			A	3.4	2.3	0.6	1.4

[a] All coupling constants are absolute magnitudes in Hz and all constants have been shown to be negative.

TABLE 6

CARBONYL BANDS IN CYCLOHEXANE

M	π- Allyl	Isomer	π-C_5H_5 $v(CO)(cm^{-1})$	K^a	π-Indenyl $v(CO)(cm^{-1})$
Mo		A	1970, 1903	≈1.0	1971, 1902
		B	1963, 1889		1963, 1887
Mo	2-Me	A	1962, 1895		1965, 1894
		B	1886[b]		
Mo	2-Cl	A	1981, 1920	≈0.5	1979, 1914
		B	1970, 1897		
Mo	2-Br	A	1983, 1921	≈0.6	1980, 1916
		B	1971, 1900		1967, 1898
Mo	1-Me	B	1953, 1879	≈2.5	1953, 1878
		A	1960, 1894		1960[b], 1890
Mo	1,3-Me$_2$	B	1945, 1872	≈4.0	
		A	1950[b], 1883		
Mo	1,1-Me$_2$	B	1949, 1874		1949, 1874
		A			
Mo	1,1,2-Me$_3$	B	1950, 1875	≈5.7	1950, 1876
		A	1960[b], 1885[b]		
W		A	1961, 1896	≈0.7	
		B	1953, 1876		
W	2-Me	A	1955, 1885		
		B	1877[b]		

[a] K is the equilibrium constant estimated from the ratio of the intensity of lower frequency(B) to that of higher frequency(A) in the π-cyclopentadienyl compounds. [b] Shoulder.

particularly pertinent since it approximates a simple AX spin case. The 1,1,2-trime-thylallyl-cyclopentadienyl derivatives show slight shoulders on the high frequency sides of the carbonyl stretching bands, a major isomer with a greater *syn–anti* coupling (2.7 > 0.6 Hz), and higher field *anti* proton resonance than the minor isomer. Hence, the predominant form in solution for the 1,1,2-trimethyl analog is assigned the B configuration.

Thermodynamic parameters and factors influencing π-allyl orientation

The difference between equilibrium constants inferred from intensities of IR carbonyl stretching bands and those from proton resonances suggested the possibility of significant solvent effects on the equilibrium constant since different solutions are used for the two techniques. The solvent effect is indeed pronounced as indicated by the following constants obtained for π-cyclopentadienyl-π-allylmolybdenum dicar-

TABLE 7

THERMODYNAMIC PARAMETERS FOR REPRESENTATIVE COMPLEXES

Compounds			Solvents	ΔH (kcal/mole)	ΔS (cal·mole^{-1}·degree^{-1})	K at 0°	K at 25°
Ring	M	2-R					
Cp	Mo	H	CHCl$_3$	-1.3 ± 0.1	-2.0 ± 0.4	4.27	3.48
			CS$_2$	-0.7 ± 0.1	-0.7 ± 0.3	2.45	2.21
Cp	W	H	CHCl$_3$	-1.7 ± 0.2	-4.4 ± 0.7	2.65	2.03
In	Mo	H	CHCl$_3$	-1.4 ± 0.2	-2.7 ± 0.8	3.27	2.65
			CH$_3$C$_6$H$_{11}$	-1.8 ± 0.3	-6.2 ± 0.9	1.30	0.98
Cp	Mo	Me	CHCl$_3$	0.8 ± 0.2	-1.5 ± 0.9	0.114	0.128
			CS$_2$	1.6 ± 0.2	0.6 ± 0.7	0.072	0.092
Cp	Mo	Br	CHCl$_3$	1.0 ± 0.2	0.2 ± 0.6	0.170	0.199
			CS$_2$	1.1 ± 0.1	1.2 ± 0.6	0.227	0.270

TABLE 8

EQUILIBRIUM CONSTANTS FOR SUBSTITUTED ALLYL COMPLEXES[a]

M	Allyl	Ring	K (B/A)[a]	Solvent	Temp. (°C)
Mo		Cp	4.27	CDCl$_3$	0°
		In	3.27	CDCl$_3$	0°
Mo	2-Me	Cp	0.11	CDCl$_3$	0°
		In	$\lesssim 0.01$	C$_6$H$_6$	5°
Mo	2-Cl	Cp	0.14	C$_6$H$_6$	5°
		In	0.01	C$_6$H$_6$	5°
Mo	2-Br	Cp	0.17	CDCl$_3$	0°
		In	0.02	C$_6$H$_6$	5°
Mo	1-Me	Cp	7.0	CS$_2$	$-10°$
		In	3.6	CS$_2$	0°
Mo	1,1-Me$_2$	Cp	$>100^b$	CDCl$_3$	0°
		In	$>100^b$	CDCl$_3$	0°
Mo	1,3-Me$_2$	Cp	17.5	CDCl$_3$	0°
Mo	1,1,2-Me$_3$	Cp	14.1	CS$_2$	$-5°$
		In	$\lesssim 50^c$	CS$_2$	$-5°$
W		Cp	2.65	CDCl$_3$	0°
W	2-Me	Cp	$\approx 0.01^d$	CDCl$_3$	0°

[a] K determined by NMR. [b] None of the resonances broaden in the range of $-10°$ to 60°. [c] All of the resonances broaden in the temperature range of 20° to 40°. Attempts to determine chemical shifts of the minor isomer by the spin saturation method were unsuccessful. [d] All the resonances broaden in the temperature range of 10° to 30°. Attempts to determine the resonance positions of the minor isomer were unsuccessful.

bonyl at $0°$; CS_2, 2.5; $CHCl_3$, 4.3; C_6H_6, 3.0. Variations with temperature were also noted; hence, enthalpy and entropy changes were determined for several representative compounds and the results summarized in Table 7. Although the entropy term is significant, one notes that large differences in equilibrium constants in the same solvent and at the same temperature reflect large differences in enthalpies. That is, when $K > 1$, then $\Delta H < 0$, and when $K < 1$, then $\Delta H > 0$. Hence, the results suggest that major differences in equilibrium constants may be attributed to intramolecular effects. Furthermore, in less interacting solvents such as cyclohexane and carbon disulfide, the equilibrium constant also indicates intramolecular energy differences. Nevertheless, it should be recognized, as in the case of the indenyl-allyl complex in cyclohexane, that ΔF can be made positive or negative when equilibrium constants are near one by variation in solvent or temperature.

Isomer B might be expected to be more polar in the alkyl-substituted allyl derivatives since less polar solvents tend to decrease K. In the 2-bromoallyl derivative, however, solution in CS_2 tends to increase K. Three trends stand out when the equilibrium constants for all of the compounds are compared by reference to Table 8. With the exception of the 1,1,2-trimethylallyl compound, all of the compounds showed a significant increase in the percentage of the A form on substitution of indenyl for cyclopentadienyl. Substitution at the 2-position of the allyl increased the percentage of A; whereas substitution at the *anti*-position drastically increased the percentage of B. It thus appears that the major contributor to the stability of a particular isomer is the relative magnitude of steric interactions between allyl substituents and the cyclopentadienyl ring.

Hence the large changes in equilibrium constant can be rationalized by assuming that two opposing steric factors principally govern the magnitude of the equilibrium constant: (1) in the A isomer interaction between the ring protons (or other ring substituents) and the *anti* substituent of the allyl ligand tends to destabilize A; and (2) in B, interaction between the ring protons and the substituent on the central carbon of the allyl moiety tends to destabilize B.

The steric effect of 2-substitution on the π-allyl. The range of validity and the degree to which equilibrium constants reflect magnitudes of steric factors is most easily determined by comparison of the cyclopentadienyl complexes of $Mo-\pi$-2-methylallyl, $Mo-\pi$-2-chloroallyl, and $Mo-\pi$-2-bromoallyl with the parent π-allyl. The 2-substituted complexes have equilibrium constants which indicate that the A configuration is favored. However, if one wishes to fully rationalize the trend in the equilibrium constants of $2-R = Br > Cl > CH_3$ in terms of steric interactions, several intermolecular distances must be considered. (1). The bond length between the central carbon of the allyl and its substituent: $C-C \approx 1.54$ Å; $C-Cl \approx 1.77$ Å; and $C-Br \approx 1.91$ Å. (2). The distance between the substituent and the cyclopentadienyl ring protons in configuration B, which is not significantly altered due to the dihedral angle expected between the allyl plane and the ring plane. (3). The effective Van der Waals' radius of the central allyl substituent: $CH_3 \lesssim Cl < Br$.

A strict correlation with Van der Waals' radii would not be expected because an increase in Van der Waals' radius is usually accompanied by an increase in covalent radius, as has been frequently observed in axial–equatorial equilibria in cyclohexane derivatives. A decrease in the dihedral angle between the cyclopentadienyl and the allyl planes would allow the increase in bond length to decrease the interaction with

the ring. Hence, [B]/[A] should be expected to decrease in the order 2-CH$_3$ > 2-Cl > 2-Br on the basis of Van der Waals' radius; however, the reverse order is observed indicating that bond-lengthening compensates for the increased substituent radius.

Nevertheless reference to Table 7 indicates that different free energies of solvation may be a major factor in the observed difference. Note that in the case of the 2-Br and 2-Cl derivatives the enthalpy differences are the reverse of the free energy differences. Enthalpy determinations, however, are insufficiently accurate to attribute significance to differences of less than a kilocalorie.

The difference in free energy upon substitution of indenyl for cyclopentadienyl was 1.5–2.0 kcal/mole. This is approximately the value of the potential well suggested for the indenyl complex. Thus the decrease in stability of the B isomer in complexes with 2-substituted allyls may well arise from the forcing of the indenyl to an angle other than 0°. This possibility is indicated by the relatively small shift of the methyl in the B isomer of the 2-methyl complex.

Generally, the cyclopentadienyl complexes exhibit an increase of free energy or enthalpy of approximately 1.5–2.0 kcal/mole attending substitution in the 2-position. Solvation effects, more subtle steric effects (such as interactions with the carbonyls), and electronic effects cause smaller changes (0.5 kcal/mole) and thus make rationalizations of less pronounced trends difficult. Despite the inability to assign the origin of the trend to a single overriding factor, the trend in K of 2-Br > 2-Cl > 2-CH$_3$ does seem to prevail in other systems.

The steric effect of 1-substitution on the π-allyl. Monosubstitution at the terminal carbon allows the possibility of *syn–anti* isomerism. In the absence of a substituent in the 2-position, the *syn* orientation is the thermodynamically more stable ($\approx 95\%$ *syn* isomers are found when *syn–anti* equilibration can take place). Hence, purification of the crotyl complex produces the *syn* isomer. Coupling constants verify the assignment of the *syn* orientation of the methyl group and therefore the possible presence of an *anti* substituent in monosubstituted allyls will be neglected in subsequent discussion*. To ensure the presence of a substituent in the *anti* position, di-substitution at the terminal allyl carbon is required. *Anti* substitution effects must then be considered relative to *syn* substituted complexes rather than the unsubstituted parent compound.

A *syn*-methyl group decreases the stability of A by ≈ 0.4 kcal/mole as indicated by comparisons of the π-crotyl to the parent allyl complex. A second *syn*-methyl further decreases the stability of A, as in the 1,3-*syn,syn*-dimethylallyl derivative. The origin of this stabilization of B, however, is certainly not dominated by steric interactions with the ring as in 2-substitution, since the direction is opposite to that expected on the basis of ring interactions. Presumably methyl–carbonyl interactions play a large role. The presence of an *anti*-methyl substituent greatly increases the stability of B (by about 1.5 kcal/mole). This effect appears to be dominated by steric interactions with the cyclopentadienyl ring.

Thus, for methyl substitution, due to effects which appear to be predominately steric in origin, the approximate changes in ΔF are to be anticipated; 2-Me $\sim +1.8$

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* Formation of the *anti* form from the *syn* form could be produced by a high energy (≈ 25 kcal/mole) π–σ–π process involving a 1-h intermediate. Within the time span of these experiments a carefully purified sample should not show the presence of the *anti* isomer.

kcal/mole; syn-Me ≈ −0.2 kcal/mole; anti-Me ≈ −1.5 kcal/mole. For alkyl substituted derivatives one can also expect a partial free energy increase of ≈0.2 kcal/mole on changing the solvent from a polar to non-polar solvent. An increase in ΔF can also be expected on 2-substitution with a halogen; but with opposite solvent effects since the polarity of the molecule is altered.

The steric effect of ring substitution. Reference to Table 7, illustrates the decrease in the stability of B with benzo substitution of the cyclopentadienyl ring in complexes without anti substituents. Although the effect is relatively small with the allyl complex, the interaction with 2-substituted allyls is particularly strong (≈1.5 kcal/mole). This follows from previous considerations, which indicated that the predominant steric factor in 2-substituted allyls was with the cyclopentadienyl ring. There is potentially a great difference in effectiveness of ring substitution due to rotation of the ring relative to the metal (vide infra).

Factors influencing the orientation of the indenyl moiety

Geometric consideration for ring current calculations. The extraordinarily large ring current effects suggest the possibility of a preferred orientation of the six-membered ring of the indenyl moiety. In order to assess the degree of orientation, it is necessary to compute theoretical values for the ring current effects and these in turn,
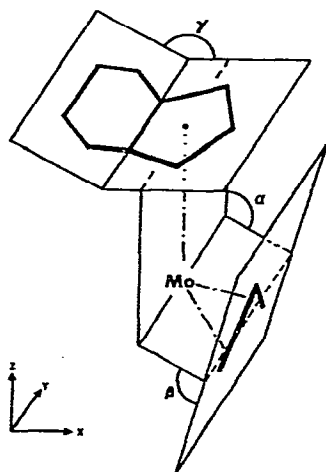
Fig. 4. Dihedral angles in the model used for magnetic anisotropy calculations.

require accurate geometrical parameters for the complex. At present, however, there is no crystallographic data for these specific complexes. We have therefore set up an approximate quantitative model with several geometric parameters to estimate the magnitude expected for various effects on the ring current calculations. This model, which is shown in Fig. 4 is based on similar complexes for which crystallographic data are available[14−18]. Although the indenyl group rotates about the five-member ring centroid–Mo axis, preliminary discussions will assume the six-membered ring to be oriented over the π-allyl, such that the molecule possesses C_s symmetry. The positions of the atoms in the entire complex can thus be determined with the assumed

angles and bond distances described in the Experimental section; hence, using standard formulae, the ring current effect on each proton can be calculated.

The origin of the chemical shift differences between the A and B isomer. Since only the allyl orientation differs in A and B in Fig. 1, no significant differences in chemical shift arising from differences in charge at the atoms would be expected. The observed shifts for the *syn* protons in both isomers are nearly the same; whereas the differences ($\delta_A - \delta_B$) for the *anti* protons are about 0.9 ppm and the central protons about −0.3 ppm. Assuming the shielding differences arise from the anisotropy associated with the cyclopentadienyl ring, one calculates the shifts shown in Table 9 if six π-electrons are taken to be equally distributed above and below the plane of the ring. Only minor effects would be expected from the π-electrons of the carbonyls, the largest being −0.1 ppm additional shift of the *syn* protons. Some improvement in the fit can also be obtained by assuming the π-electrons to be displaced toward the metal and by adjusting the α and β angles. Nevertheless, the fact that the signs and approximate magnitudes of the shift differences can be reproduced, suggests the presence of a major contribution from the magnetic anisotropy of the metal–ring system.

TABLE 9

CALCULATED DIFFERENCES IN CHEMICAL SHIFTS FOR A AND B ISOMERS IN π-C$_5$H$_5$-π-C$_3$H$_5$Mo(CO)$_2$[a]

Ring π-electron position (A)	Carbonyl π-electron contribution (e)	Allyl angle $\beta(A)$ (°)	$\delta_A - \delta_B$ (ppm)		
			H_c	H_{syn}	H_{anti}
Calculated					
0.0	0	70	−0.40	−0.12	+0.41
0.0	0	65	−0.36	−0.11	+0.42
0.3	0	70	−0.54	−0.16	+0.69
0.3	0	65	−0.48	−0.15	+0.71
0.0	4	70	−0.38	−0.20	+0.48
Observed (in chloroform)					
			−0.34	−0.06	+0.88

[a] The details of the calculation are discussed in the text. The assumed geometric parameters are Mo−Ps= 2.3 Å; $\alpha = 113°$; $\beta(B) = 180° - \beta(A)$.

The calculated effect of the ring current on the ^{13}C resonances is less than 0.2 ppm; nevertheless, the difference of −3.5 ppm for the terminal carbon and 18.5 ppm for the central carbon is substantial. Since significant differences in bond polarity in the two isomers is not anticipated, we attribute the variations in chemical shift to differences in the degree of twisting of the terminal methylenes out of the allyl plane in the two isomers*.

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* In the structure of π-cyclopentadienyl-π-benzylmolybdenum dicarbonyl, the terminal methylene appears to be distorted out of the plane[14].
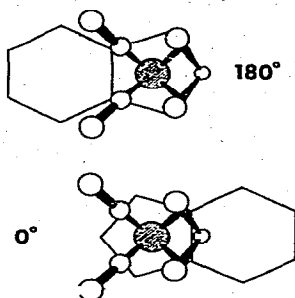
Fig. 5. Two conformations of the indenyl ligand. The angle θ defines rotation of the indenyl group about an axis between the five-membered ring and the metal.

Fig. 6. The effect of orientation of the π-indenyl group on the chemical shift of π-allyl protons: *top*, central proton in B; *bottom*, *anti* protons in A. The calculation indicates only the magnetic anisotropy associated with the six-membered ring of the indenyl group. The following parameters were used: Mo–Ps = 2.3 Å: $\alpha = 113°$; $\gamma = 180°$; $\beta(\text{B}) = 70°$; $\beta(\text{A}) = 110°$.
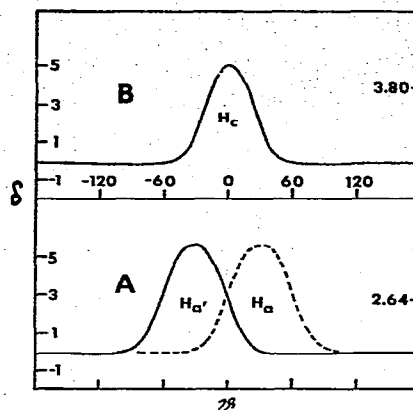
The origin of the chemical shift differences between π-cyclopentadienyl and π-indenyl complexes. The large differences observed in the chemical shifts of the allyl protons in indenyl complexes, as compared to cyclopentadienyl complexes, may be readily ascribed to the ring current effect of the additional six-membered ring in the indenyl moiety. The possibility of different orientations (see Fig. 5) of the six-membered ring of the indenyl must be considered, since the indenyl group would be expected to have relatively free rotation about the Mo–five-membered-ring axis. Fig. 6 shows the calculated chemical shift due to the ring current as a function of orientation. This calculation assumes six π-electrons in the benzo-ring and both rings are assumed to lie in the same plane ($\gamma = 180°$ in Fig. 4). This calculation should thus allow a good comparison of the shifts of the indenyl complex to those of the cyclopentadienyl complex, since the other factors contributing to the shifts should be essentially the same in both complexes. Experimentally, the relative shift of the *anti* protons of the A isomer is 2.64 ppm and that of the central proton of the B isomer is 3.80 ppm. If all orientations of the indenyl ligand were equally probable and rotation of the ligand were rapid enough to average the shifts for each individual orientation, the averaged relative shift would only be 0.90 ppm for the *anti* protons in A and 0.61 ppm for the central proton in B.

Although fairly large errors in the calculated ring current might be expected on the basis of the number of assumptions involved, an error of this magnitude is extremely unlikely. It thus appears that there is a preference for orientation of the six-membered ring toward the side of the allyl ($\theta \approx 0°$), *i.e.* as shown in Fig. 2.

The intramolecular rotation of a π-cyclopentadienyl group usually has a very low potential barrier*, and the simplest potential energy diagram might be represented

* Broad line NMR and electron diffraction studies indicate barriers of approximately 1–3 kcal/mole[19-21].

TABLE 10

THE EFFECT OF THE POTENTIAL WELL DEPTH ON THE CHEMICAL SHIFT DIFFERENCES BETWEEN π-INDENYL- AND π-CYCLOPENTADIENYL-π-ALLYLMOLYBDENUM DICARBONYL[a]

Potential (kcal/mole)	Central proton		Syn protons		Anti protons	
	A	B	A	B	A	B
72° well						
0.0	0.24	0.61	0.28	0.37	0.90	0.33
1.0	0.33	1.76	0.35	0.47	1.45	0.41
2.0	0.46	3.48	0.44	0.59	2.21	0.51
3.0	0.54	4.49	0.48	0.65	2.62	0.57
∞	0.57	5.04	0.49	0.63	2.72	0.58
360° well						
1.0	0.34	1.32	0.42	0.61	1.64	0.45
2.0	0.42	1.95	0.50	0.76	2.16	0.52
3.0	0.46	2.42	0.53	0.82	2.44	0.56
4.0	0.48	2.75	0.54	0.84	2.59	0.57
∞	0.57	5.04	0.49	0.63	2.72	0.58
Experimental						
	0.21	3.80	−0.74	0.46	2.64	−0.08

[a] Geometric parameters assumed were: Mo–Ps = 2.30 Å; $\alpha = 113°$; $\beta(A) = 70°$; $\beta(B) = 110°$; $\gamma = 180°$.
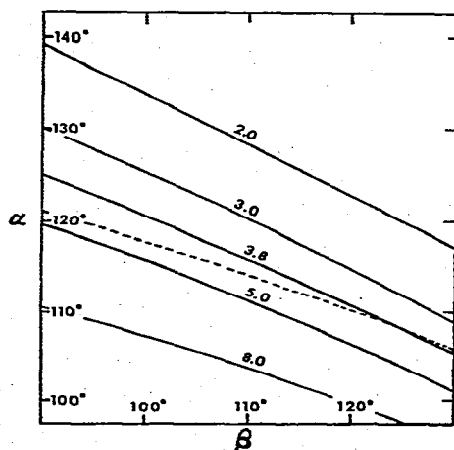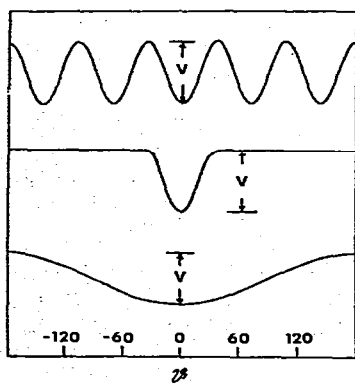
Fig. 7. Simplified potential functions for orientation of cyclopentadienyl and indenyl ligands: *upper*, five-fold well; *middle*, 72° well; *lower*, 360° well. The depth of the well is V and appears to lie in the range 1–5 kcal/mole in these compounds. The lack of five-fold or cylindrical symmetry in the Mo(CO)₂ (allyl) segment makes the curves particularly crude approximations; nevertheless, five equally spaced minima in the upper curve would be expected for the cyclopentadienyl derivatives.

Fig. 8. The effect of dihedral angle on chemical shift of the central proton of the B configuration of π-indenyl-π-allylmolybdenum dicarbonyl. The solid lines connect points of equal chemical shift (ppm). The broken line connects points which correspond to a central carbon–molybdenum distance of 2.3 Å. The calculation assumes $\theta = 0°$ and $\gamma = 180°$.

as a 5-fold cosine well. The introduction of the six-membered ring in the indenyl complex makes the potential more complicated. To simplify the calculation we have assumed that the π-cyclopentadienyl group freely rotates and that a single symmetrical well based on a cosine function exists with its minimum at $\theta = 0°$. Well-widths of 72° and 360° were considered giving the potential functions as shown in Fig. 7. The effects on the chemical shifts are indicated in Table 10. The wider the well, the deeper it must be to produce the same effect. Considering the approximations it is premature to speculate about the nature of the potential functions; nevertheless, we feel that the model is sufficiently reliable to indicate the presence of a well-depth of at least 2 kcal/mole, for each isomer.

The expected well-depth is not significantly altered by adjustment of the geometric parameters, although the shifts are sensitive to them. The negative shift of the A *syn* protons represent the only significant discrepancy in the calculated values. We believe that this discrepancy arises from twisting of the protons out of the plane of the allyl and uncertainty in the α and γ angle*.

Although there are many adjustable parameters, α and β must be kept within limits which maintain a reasonable metal-to-central carbon distance and reasonable ring–allyl proton Van der Waals' contacts. Fig. 8 illustrates the effect of varying α and β assuming a fixed orientation of the indenyl at $\theta = 0°$. A chemical shift difference of 3.8 ppm corresponds to a distance to the six-membered ring of 2.0 to 2.3 Å. For $\alpha = 113°$ and $\beta = 110°$ the distance between the central proton and the six-membered ring plane is 2.0 Å, and the predicted chemical shift difference is 4.5 ppm.

Thus, a potential minimum for the B isomer at $\theta = 0°$ is implied. A somewhat broader minimum for the A isomer centered at $\theta = 0°$, possibly even developing to a double minimum, is anticipated.

The origin of the potential well. An attractive force between the six-membered ring in the indenyl group and the allyl, such as hydrogen bonding or a weak bonding interaction between the π-orbitals of both groups, could be the source of the preference for indenyl orientation at $\theta = 0°$. An orientation providing maximum bonding interaction by the metal with a combination of π-allyl–π-olefin bonds instead of π-cyclopentadienyl-type bonds appears to be a more likely rationale for the preference.
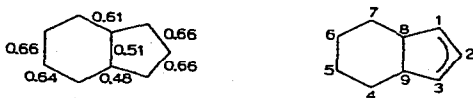
Huckel calculations show for both the nine and ten electron C_9H_7 system the highest π-bond order for the five-membered ring lies between the 1–2 and the 2–3 positions. This suggests a π-allyl-bonding description between 1, 2, and 3 may be appropriate**. Any attempt to accurately describe the bonding must consider symmetry properties

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* Only one structure of a π-indenyl complex has been obtained, *i.e.* $C_9H_7Mo(CO)_3I$. Although it is suggested that there is not significant deviation of the six-membered and five-membered rings from co-planarity[23], the data are sufficiently poor that $\gamma = 175°$ could be within experimental error. In more accurate structures of coordinated fused-ring systems significant deviations from coplanarity are observed[22,24].

** In π-$C_9H_7Mo(CO)_3I$ the indenyl system does not have a plane of symmetry[23], the average bond lengths corresponding to those in the structure proposed for the allyl derivatives are: 1–2, 1.39 Å; 1–8, 1.53 Å; 8–9, 1.50 Å; 4–9, 1.39 Å; 4–5, 1.45 Å; and 5–6, 1.48 Å.

and interaction with antibonding orbitals. We would be led too far afield by such a discussion at this point; nevertheless, suffice it to say that the presence of the six-membered ring forces changes in the dimensions, charge distributions, and molecular orbitals of the five-membered ring. We propose that sufficient asymmetry results from the bonding of the allyl and carbonyl groups on the opposite side of the molybdenum atom to provide an orientational preference of the indenyl moiety via differing degrees of interaction of indenyl orbitals with the molybdenum-containing fragment as a function of orientation. The influence of the asymmetry of the rest of the ligands attached to the metal on the dimensions of the ring is amply demonstrated in the structure of $(C_5H_5)_3MoNO$ and $(C_5H_5)_2(CH_3)MoNO$, in which formally h^5-rings are significantly distorted from 5-fold symmetry[25]. In this case the rings can rotate about the metal–ring axis with the bond lengths in the ring adjusting to the most stable arrangement every 72°. The presence of the six-membered ring in the indenyl forces an increased double bond character between the 1, 2, and 3 carbons; hence the dimensions of the five-membered ring cannot be optimized with every rotation of 72° as with cyclopentadienyl ligands. Thus, several minima of varying depths, depending on the compatibility of the five-membered ring with the optimum dimensions, would be anticipated.
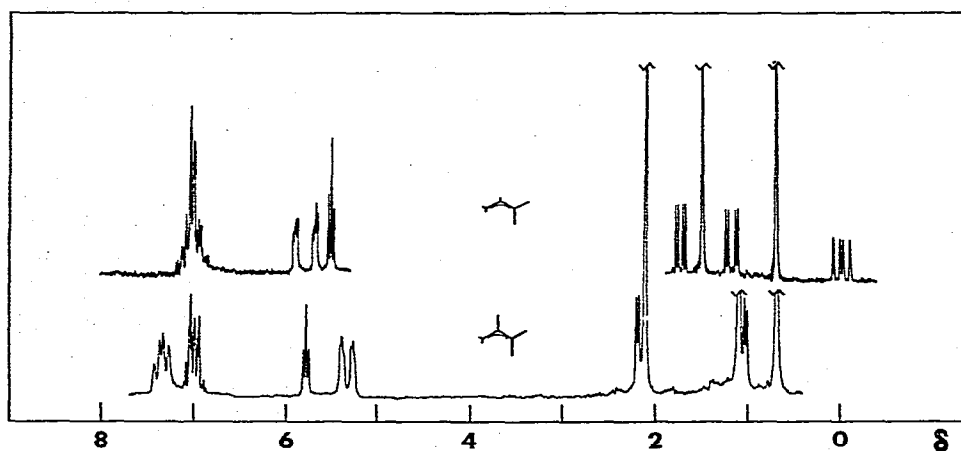

Fig. 9. The 100 MHz proton resonance spectra of π-indenyl-π-(1,1-dimethylallyl)molybdenum dicarbonyl *upper*, and π-indenyl-π-(1,1,2-trimethylallyl)molybdenum dicarbonyl *lower*, in carbon disulfide.

The effect of the allyl substituents on ring orientation. The major factor in determining the orientation of the allyl was shown to be interaction with the five-membered ring or its substituents, which indicates a substantial steric interaction between the indenyl ligand and the substituents on the allyl. Through most of the series studied the large upfield shifts of certain allyl protons demonstrated that the orientation of $\theta \approx 0°$ was preferred. It appears, however, that angles other than zero are more probable in the 1,1,2-trimethylallyl derivative.

The shifts generally observed are exemplified by the spectrum of the 1,1-dimethylallyl complex shown in Fig. 9. This species exists almost entirely in the B configuration due to the presence of the *anti*-methyl group and the characteristic shift of the

central allyl proton to $\delta \approx 0$ is observed. In all cases except the 1,1,2-trimethylallyl derivative, the 1,3-indenyl protons are shifted downfield of the 2-proton. Since the $Mo(CO)_2$ (allyl) fragment is chiral when the allyl is unsymmetrically substituted, the 1- and 3-protons of the indenyl show different chemical shifts; nevertheless, both still appear below that of the 2-proton.

Thus, it is unusual to find in the spectrum of the 1,1,2-trimethylallyl derivative that the 1,3-protons of the indenyl are shifted ≈ 0.5 ppm above the 2-proton instead of below; that the 4,7- and 5,6-protons are shifted nearly 0.3 ppm instead of being nearly equivalent; that the *anti* 1-methyl group resonances shifted to a lesser degree than expected ($\delta_{anis} \approx +0.8$ ppm experimental compared to between 1.5–2.0 calculated for $\theta = 0°$); and that the *anti* protons in both isomers show nearly the same chemical shift*.

These effects may be attributed to a preference for a different orientation of the indenyl moiety relative to the allyl, which arises from increased steric interaction of the six-membered ring with the allyl due to the presence of the *anti* methyl group.

These steric interactions are sufficient to destabilize the $\theta = 0°$ orientation by more than 2 kcal/mole; hence, other orientations become equally, if not more probable. This change in preferred orientation should have a profound effect on the equilibrium constant between the A and B configurations with bulky substituents in both *anti* and *central* positions respectively. This effect is noted for the 1,1,2-trimethylallyl (Table 7) which shows a four-fold increase in B/A on indenyl substitution compared to over ten-fold increases in A/B in other allyls. Thus when non-zero θ angles are dominant, the interaction with the indenyl ring decreases and A/B ratios would be expected to be closer in the cyclopentadienyl and indenyl complexes.

Coupling constants and geometry

Whereas most of the coupling constants are nearly identical in both isomers, the geminal coupling is characteristically more than 1.0 Hz greater in magnitude in the B configuration than in the A configuration. Tables 3 and 5 give the magnitude of the coupling constants, but relative signs were determined by double resonance studies. The *geminal* constant, J_{sa}, was shown to have the opposite sign of J_{ca} and J_{cs} in all of the complexes where it could be measured. The absolute signs of *cis* and *trans* vicinal couplings in vinyl derivatives are considered positive on the basis of experiment and theory[26]; therefore, we assume that J_{ca} and J_{cs} in the allyl complex, which have approximately the same magnitudes as in the vinyl cases, are positive. Thus, J_{sa} is negative in all of these allyl complexes.

Alkyl substituted ethylenes show *geminal* coupling constants of approximately $+2.0$ Hz, whereas the protons at 109° in methane give rise to a large negative constant of -12 Hz[26,27]. Differences in substituent electronegativity can cause variations, but are not expected here because the *vicinal* couplings are not unusual. Thus, we believe that distortions of the *geminal* protons out of the plane of the allyl carbon atoms are responsible for the variations in *geminal* coupling.

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* Although it was not possible to directly observe the resonances of the A isomer (Table 2), the positions relative to the those of the B isomer can be deduced by considering the broadening observed for each B isomer resonance as a function of temperature. The maximum additional broadening (in Hz) observed for each resonance is as follows: 1.06 (5); 2.08(3); 2.16(8); 0.65(< 2); 0.99(1). Using an equilibrium constant of 50, line shape calculations indicate that the A isomer resonances must be displaced by shifts (ppm) of approximately the following magnitude: c-CH_3, 2.4; s'-CH_3, 1.9; s-H, 3.8; a'-CH_3, < 0.9; a-H, 0.5.

TABLE 11

FREE ENERGIES OF ACTIVATION FOR π-ALLYL COMPLEXES

M	π-Allyl	Ring	Solvent	$\Delta F^*(A{\rightarrow}B)$ (kcal/mole)	$k(25°)$ (sec^{-1})	$\Delta F^*(B{\rightarrow}A)$ (kcal/mole)	$k(25°)$ (sec^{-1})
Mo		Cp	CDCl$_3$	15.2±0.1	45±5	16.0±0.1	12±1
			C$_6$D$_{12}$	15.4±0.1	31±4	15.9±0.1	14±1
			CS$_2$	15.4±0.1	35±4	15.8±0.1	16±2
Mo		In	CDCl$_3$	16.2±0.2	9±2	16.8±0.2	4±1
			MeC$_6$H$_{11}$	16.7±0.1	4±1	16.7±0.1	4±1
W		Cp	CDCl$_3$	15.3±0.1	38±5	15.6±0.1	20±2
			C$_6$D$_{12}$	15.5±0.1	27±3	15.5±0.1	25±2
Mo	2-Me	Cp	CDCl$_3$	16.1±0.1	10±1	15.0±0.1	60±10
			CS$_2$	16.1±0.1	10±1	14.8±0.1	90±10
Mo	2-Br	Cp	CDCl$_3$	16.5±0.1	5±1	15.7±0.1	21±1
			C$_6$D$_{12}$	16.4±0.1	6±1	15.7±0.1	20±1
			CS$_2$	16.3±0.1	7±1	15.5±0.1	28±2
Mo	1,3-Me$_2$	Cp	CS$_2$	15.3±0.2	40±12	17.0±0.2	2±1
Mo	1,1,2-Me$_3$	Cp	CS$_2$	14.8±0.2	90±30	16.3±0.2	7±3

Isomer interconversion

Temperature not only affects the population ratio of the A and B isomers but also changes the rate of interconversion between them. At lower temperatures ($< 0°$) the interconversion rate is slow on the NMR time scale and the spectrum shows resonances corresponding to both isomers. There are no significant changes other than changes in relative intensities as the temperature is decreased further. At high temperatures ($>65°$) the interconversion rate is fast, and the NMR spectrum appears as the average of the resonances of the separate isomers. At temperatures between these two limits the NMR spectrum shows broadening and coalescence of the lines, and rates can be calculated from computed line shapes. The free energies of activation, determined at temperatures where accurate rate data could be obtained, are reported in Table 11. Replacement of cyclopentadienyl by indenyl generally results in an increase of approximately one kcal/mole in ΔF^*. This can presumably be attributed to increased steric interaction in the intermediate or transition state. Comparison of substituted derivatives requires additional consideration of variations in ground state energies. Major differences are not observed between the unsubstituted and 2-substituted allyls, although bromo substitution causes a slight increase in the barrier. Steric interactions in the transition state appear to be responsible for the significant increase in barrier observed upon substitution on both terminal carbon atoms*.

Since *syn* and *anti* protons are not averaged during isomer interconversion, what is effectively a rotation of the planar allyl about an axis between the metal and the center of gravity of the allyl appears most reasonable**. This apparent rotation of

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* The barriers are sufficiently high in the indenyl complex that the configuration in the solid state can be determined. Upon dissolving crystals of π-indenyl-π-allylmolybdenum dicarbonyl in methylene chloride at $-70°$ only resonances of the B configuration are seen in the PMR spectrum. Resonances corresponding to A gradually appear in the spectrum upon standing at $-70°$; thus, B is the configuration in the crystalline material melting at 119–121°.

** A detailed discussion of π–σ–π rearrangements, rotation and pseudorotation in these complexes, π-benzyl complexes, and tripyrazolylborate complexes will be the subject of a future publication.

the allyl group about an axis to the metal is relatively rare.

Rearrangement mechanisms of compounds containing four ligands in addition to the cyclopentadienyl group and having the general formula π-$C_5H_5Mo(CO)_2LR$ have been studied extensively[28]. The lowest energy pathway for *cis–trans* isomerism appears to involve an intermediate approximating a trigonal bipyramid with the C_5H_5 ring occupying one apical position and either R or L occupying the other. The *trans–cis* barrier is strongly dependent on the nature of R (R=H$\approx$13 kcal/mole; R=I$\approx$26 kcal/mole) and similar effects may account for variations in barrier in the allyl complexes. We find it convenient to consider the transition state or intermediate for the interconversion of A and B allyl isomers as an approximate trigonal bipyramid with the cyclopentadienyl ring at one apex and an end of the allyl at the other apex. Since the allyl group is merely a chelating ligand attached to a system which has already been shown to be stereochemically nonrigid, it follows that the allyl complex should also be nonrigid. Thus, we prefer to consider the interconversion of the B and A isomers as a pseudorotation due to the nonrigidity of parent π-$C_5H_5Mo(CO)_2LR$ structure, rather than as a rotation about an allyl metal axis*. With this view of the A–B interconversion, one would generally expect that a parent system which showed no stereochemical nonrigidity, would not show "rotation" of the allyl. For example, the π-$C_5H_5(CO)FeLR$ group has been shown to be a rigid structure with respect to the chirality of the iron on the NMR time scale[29]. Consequently, "rotation" of the allyl group would not be anticipated. For example, King and Ishaq have shown that the analogs of the A and B isomers in π-C_5H_5-π-$C_3H_5Ru(CO)$ exist and do not interconvert rapidly[30].

CONCLUSION

The control of the ratio of the two isomers of π-cyclopentadienyl-π-allyl-molybdenum dicarbonyl has been shown to be predominantly steric in origin. Substitution on the central carbon of the allyl tends to shift the equilibrium toward B. The replacement of the π-cyclopentadienyl group by π-indenyl generally increases the steric interactions and causes pronounced changes in certain equilibria. In most cases the indenyl group occupies a preferred conformation with the six-membered ring oriented over the allyl moiety; however, *anti*-substitution in the A isomer offers sufficient steric hindrance to make other conformations more probable.
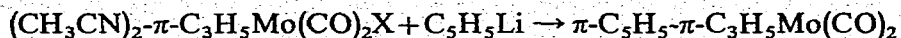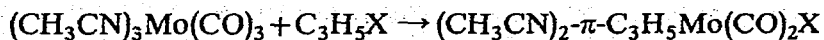
EXPERIMENTAL

Preparation of complexes

The preparations of π-C_5H_5- and π-C_9H_7-π-$C_3H_5Mo(CO)_2$ are similar and are based on the procedure of Hayter[31]. The following reactions were carried out under a nitrogen atmosphere.

$$CH_3CN + Mo(CO)_6 \rightarrow (CH_3CN)_3Mo(CO)_3$$

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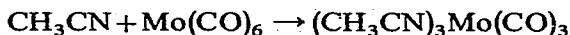
* This should not be construed as an attempt to accurately describe the geometry of the transition state or the exact path each atom follows during the interconversion. It is suggested merely as an alternative way of considering the mechanism which has distinct advantages.

$$(CH_3CN)_3Mo(CO)_3 + C_3H_5X \rightarrow (CH_3CN)_2\text{-}\pi\text{-}C_3H_5Mo(CO)_2X$$

$$(CH_3CN)_2\text{-}\pi\text{-}C_3H_5Mo(CO)_2X + C_5H_5Li \rightarrow \pi\text{-}C_5H_5\text{-}\pi\text{-}C_3H_5Mo(CO)_2$$

The molybdenum hexacarbonyl was refluxed for approximately 2 h in acetonitrile until it no longer sublimed out of the solution. The yellow solution was cooled to room temperature and 1.5 to 2 times the molar quantity of the appropriate allylic halide was added. This mixture was stirred at 60° for 18 h, after which time cooling to room temperature was usually accompanied by the precipitation of the desired product, $(CH_3CN)_2\text{-}\pi\text{-}C_3H_5Mo(CO)_2X$. A tetrahydrofuran solution of the molybdenum complex was mixed with an equimolar tetrahydrofuran solution of cyclopentadienyllithium or indenyllithium* stirred for 18 h at room temperature. The solvent was removed and the viscous brown residue transferred to an acid-washed alumina column using tetrahydrofuran. The product was eluted either with petroleum ether or a 1/1 mixture of ether/petroleum ether. The complexes, all of which are yellow, were recrystallized from ether/hexane mixtures.

The compounds are slightly soluble in petroleum ether and soluble in ether, benzene, carbon disulfide, and polar organic solvents. They can be stored without significant decomposition as solids under a nitrogen atmosphere and refrigeration for months. The melting points of the complexes are listed in Table 12.

TABLE 12

MELTING POINTS (°C) OF π-ALLYL COMPLEXES

Metal	π-Allyl	π-C_5H_5	π-C_9H_7
Mo		165–168	119–121
Mo	2-Me	79– 81	117–118
Mo	2-Cl	108–109	95– 98
Mo	2-Br	101–102	136–140
Mo	1-Me	73– 76	109–111
Mo	1,1-Me$_2$	65– 69	117–118
Mo	1,3-Me$_2$	146–148	
Mo	1,1,2-Me$_3$	140–143	76– 78
W		184	
W	2-Me	103–105	

The geometric model

The crystal structures of several formally seven-coordinate complexes with the general formula π-$C_5H_5Mo(CO)_2LR$ have been determined[16–18]. Considering these structures and particularly the π-cyclopentadienyl-π-benzylmolybdenum dicarbonyl the geometric model for the compounds is shown in Fig. 4 and assumes the following values for the π-$C_5H_5Mo(CO)_2$ moiety:

(1). The carbon atoms of the π-cyclopentadienyl ring are taken to be at the corners of

* The cyclopentadiene monomer was treated with an equimolar amount of n-butyllithium in anhydrous ether to form cyclopentadienyllithium. The ether solvent was removed under oil pump vacuum and the salt was dissolved in dry tetrahydrofuran. The indene can directly be treated with n-butyllithium in anhydrous ether to form indenyllithium.

a pentagon with a distance to the centroid of 1.21 Å.

(2). The perpendicular distance between the Mo atom and the π-C_5H_5 plane is taken as 2.02 Å, and the Mo atom is assumed to be equidistant from each carbon atom.

(3). The molybdenum to carbonyl-carbon bonds are assumed to be linear, and the Mo–C and C–O distances then are 1.97 and 1.16 Å respectively.

(4). The ring centroid to Mo to CO angle is taken as 120° and the OC–Mo–CO angle is taken as 78°.

The geometry of the fragment described above is considered to be relatively independent of the orientation of the allyl in the A and B configuration; the orientation of the allyl plane relative to this fragment, however, requires further consideration. An adequate model for the A configuration is available by reference to π-cyclo-pentadienyl-π-benzylmolybdenum dicarbonyl, which has a π-allyl type structure. No B configurations have yet been reported. References to allyl–palladium complexes[15], however, provide some indication of the dihedral angle to be expected between the metal and the allyl plane. The π-allyl ligand in dimeric π-allylpalladium chloride forms a plane which makes a 68.5° dihedral angle with the planar $PdCl_2Pd$ bridge system. The C–C–C bond angle is about 128° and the terminal carbon atoms are about 0.1 Å below the $PdCl_2Pd$ plane while the central carbon is about 0.4 Å above the plane. In order to transfer the π-allyl structure to the molybdenum system, we assume two pseudo atoms (Ps) to be located four-fifths of the distance along the carbon–carbon bonds from the central carbon. Taking the y axis parallel to the π-allyl ligand plane and assuming the π-cyclopentadienyl ring to lie in the xy plane; the angle between the yz plane and the plane containing the Mo and the two Ps is α (see Fig. 4). The angle between the Ps–Mo–Ps plane and the π-allyl plane is β. For both isomers α is $\approx 113°$; whereas, β is $\approx 110°$ for A* and $\approx 70°$ for B using the analogy to the palladium systems. The bond distance between the Mo and the Ps is taken as 2.30 Å.

Within the π-allyl group all of the hydrogen atoms are assumed to lie in the plane of the carbon atoms. Crystal structures[15–18] indicate that there is less than 0.03 Å displacement out of the carbon plane; and that C–H bond distances of 1.08 Å and H–C–H bond angles of 122° should be used. Deviations of less than 0.05 Å in bond lengths and less than 5° are expected in the C–C–C and H–C–H angles. Thus in estimating the magnitude of ring currents, we have kept the structure of the π-allyl group fixed and varied the two parameters, which are most significant in displacing the protons of the π-allyl group relative to a fixed position of the cyclopentadienyl or indenyl ligand.

In the indenyl case, the distance between the center of the five-membered ring and the center of the six-membered ring is taken as 2.42 Å. The angle between the five- and six-membered ring planes is γ, which is assumed to be $\sim 175°$.

Instrumentation

IR spectra of cyclohexane solutions of all compounds were measured. A Perkin–Elmer 421 grating instrument was used with calibration from DCl. Carbonyl stretching frequencies are accurate to ± 1 cm^{-1}.

PMR spectra were obtained using a Varian Associates HA-100 spectrometer operating in frequency sweep mode. The probe temperature for kinetics experiments

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* The angles for A are more reliable since they are based on crystal structure of the benzyl complex.

were measured by means of a copper–constantan thermocouple. Temperatures requiring less precision sometimes used an alternative calibration procedure based on the variation in chemical shift between the methyl and hydroxyl protons in methanol with temperature.

Kinetics

The pseudo-first-order rate constants for leaving a given site were determined from the broadening of the resonance assigned to that site from the equation:

$$k = \pi \cdot (\Delta v'_{\frac{1}{2}} - \Delta v_{\frac{1}{2}}) \qquad (1)$$

where $\Delta v'_{\frac{1}{2}}$ and $\Delta v_{\frac{1}{2}}$ refer to the full widths of the resonances at halfheight in the presence and absence of exchange, respectively. Kubo–Sack line shape methods were used when large population differences existed and have been discussed elsewhere[29].

Free energies of activation were calculated from:

$$\log k = 10.321 + \log T - \Delta F^*/2.303R \cdot T \qquad (2)$$

using the line-broadening equations above. This equation requires only one rate constant at one temperature to evaluate ΔF^*. Temperatures were selected which allowed the greatest precision in the measurement of the broadening. That is, the temperature was adjusted such that the exchange broadening $(\Delta v'_{\frac{1}{2}} - \Delta v_{\frac{1}{2}})$ was between 2.0 and 5.0 Hz. After temperature equilibration was attained, the rates determined at that temperature varied over a range of less than $\pm 10\%$ and standard deviations of the broadening were less than ± 0.1 Hz. A $\pm 10\%$ range in rate constant corresponds to approximately a 0.03 kcal/mole range in ΔF^*. Furthermore, over a $\pm 5°$ range of temperature the reported values of ΔF^* never varied by more than ± 0.1 kcal/mole.

Although the precision of the method allows significance to be attached to differences of 0.3 kcal/mole under identical conditions; errors arising from variations in natural line widths and populations; overlap of resonances, approximations of chemical shift differences and errors in temperature measurement suggest that the accuracy of the method is less. That is, the differences in ΔF^* determined at a given temperature are significant; however, the uncertainty in the absolute magnitude of ΔF^* might be as large as ± 0.5 kcal/mole. In cases where it has been possible to measure rates over a range of temperature of 150°, log A values of 12.8 have generally been observed for intramolecular first-order reactions. Hence, E_a can be computed approximately assuming this value of log A and it is found that E_a and ΔF^* are quite similar. We have found that attempts to determine activation parameters from Arrhenius plots of rates determined from NMR data obtained over a very narrow temperature range generally give very misleading results; hence we have chosen to restrict our rate studies to determinations of ΔF^*.

The rate constants at 25° were calculated from eqn. (2) from the ΔF^* values. The rate data which were obtained are listed below with the temperature (°C), k_{AB} and k_{BA} (sec^{-1}).

π-Cyclopentadienyl-π-allylmolybdenum dicarbonyl. In CDCl$_3$: 11.8, 12, 3; 20.0, 32, 8.3. In C$_6$D$_{12}$: 16.9, 14.5, 6.5; 27.3, 38, 17. In CS$_2$: 2.9, 6.4, 2.6; 11.5, 9.8, 4.2.

π-Indenyl-π-allylmolybdenum dicarbonyl. In CDCl$_3$: 35.4, 26, 11; 48.5, 83, 37. In MeC$_6$H$_{11}$: 30.7, 5, 5; 37.6, 9, 9.

π-Cyclopentadienyl-π-allyltungsten dicarbonyl. In CDCl$_3$: 4.5, 6.3, 2.7; 15.0,

14.8, 7.2; 72.5, 1320, 1180. In C_6D_{12}: 11.0, 7.4, 6.6; 19.4, 32, 28; 51.3, 240, 210; 60.3, 290, 260.

π-*Cyclopentadienyl-π-(2-methylallyl)molybdenum dicarbonyl.* In $CDCl_3$: 10.4, 0.75, 14; 27.4, 6.5, 120; 32.4, 18, 340; 66.7, 28, 520. In CS_2: 3.5, 1.1, 14; 14.4, 3.0, 33; 31.3, 17.5, 160.

π-*Cyclopentadienyl-π-(2-bromoallyl)molybdenum dicarbonyl.* In $CDCl_3$: 16.5, 2.2, 8.8; 26.2, 5.2, 21; 34.5, 13, 52; 43.5, 30, 120; 75.6, 260, 940. In C_6D_{12}: 17.5, 2.9, 9; 20.7, 4.4, 14; 28.0, 8.5, 27; 31.5, 12, 39; 37.2, 19, 61; 55.5, 51, 159. In CS_2: 15.3, 2.8, 11; 25.8, 11.7, 43.

Thermodynamics

Equilibrium constants were determined at several temperatures by weighing traces of the resonances. The percentage of the isomers obtained by these methods are believed to be correct within 1 %. A least-squares fit of $\ln(K)$, where $K = [B]/[A]$, versus $1/T$ gave ΔH and ΔS between isomers. These values for the enthalpy difference and the entropy difference are not very accurate; however, they are quite adequate for reproducing an accurate value of K at desired temperatures.

The equilibrium constant data are listed below with the temperature and K.

π-*Cyclopentadienyl-π-allylmolybdenum dicarbonyl.* In $CDCl_3$: -57.1, 7.35; -48.4, 7.30; -33.7, 6.63; -30.6, 6.27; -21.0, 5.59; -11.4, 4.33; -1.3, 4.15; 11.8, 3.72; 16.0, 3.83; 20.0, 3.62; 21.5, 3.55. In CS_2: -31.8, 2.88; 2.9, 2.42.

π-*Indenyl-π-allylmolybdenum dicarbonyl.* In $CDCl_3$: -41.6, 4.84; -28.7, 4.60; -15.2, 3.83; -2.6, 3.79; 10.1, 2.76; 26.4, 2.55.

π-*Cyclopentadienyl-π-allyltungsten dicarbonyl.* In $CDCl_3$: -62.1, 6.15; -41.4, 5.09; -32.1, 4.53; -22.0, 3.74; -18.5, 3.16; -10.1, 2.68; 3.8, 2.61; 4.5, 2.43.

π-*Cyclopentadienyl-π-(2-methylallyl)molybdenum dicarbonyl.* In $CDCl_3$: -56.0, 0.80; 4.2, 0.112. In CS_2: -40.3, 0.044; -3.9, 0.069.

π-*Cyclopentadienyl-π-(2-bromoallyl)molybdenum dicarbonyl.* In $CDCl_3$: -42.8, 0.117; -36.2, 0.127; -23.7, 0.142; -12.1, 0.169; -1.1, 0.158; 9.3, 0.180. In C_6D_{12}: -26.3, 0.17; -13.2, 0.21; -3.0, 0.25; 12.0, 0.265; 13.6, 0.275; 17.5, 0.31. In CS_2: -47.2, 0.145; -2.8, 0.222.

NMR parameters

The spin–spin coupling constants were obtained directly from the splittings observed in the spectra in 1-substituted allyl complexes. The coupling constants for 2-substituted allyl compounds in Table 5 were obtained from the calculations of AA'-BB' type spectra and comparison to the experimentally observed spectra. The computer programs of the NMR spectrum analysis were originally written by Bothner-By for up to 5-spin systems[32]. The set of coupling constants were varied, and the best fit of calculated splittings and intensities, as determined by trial and error, are reported in Table 5.

The relationships between the observed splittings and coupling constants are[33]:

$$N = J_{as} + J_{as'}$$
$$K = J_{ss'} + J_{aa'}$$
$$M = J_{ss'} - J_{aa'}$$
$$L = J_{as} - J_{as'}$$

Since the N and K values can be obtained most accurately from the experimental spectra, these values were fixed and M and L values were varied to optimize correspondence with the observed spectra. We have also assumed that $|J_{as}| > |J_{as'}|$ and $|J_{ss'}| > |J_{aa'}|$ on the basis of comparison with allyls having other substitution patterns. The latter assumption is also verified by ^{13}C satellites in the PMR of the *syn* protons in both the parent allyl and the 2-methylallyl, which show $J_{ss'} \approx 3$ Hz.

Magnetic anisotropy calculations

The local magnetic field induced by an external field in an aromatic ring system usually makes the observed chemical shifts deviate widely from their expected positions. A quantitative parameterization of this effect in terms of a ring current, which reproduces experiment, has been developed by Johnson and Bovey[34]. The π-electrons in an aromatic ring are considered to move in circular loops above and below the plane of the carbon atoms. The induced magnetic field arising from the circulation of the electrons allow the change in chemical shift at a particular position relative to the ring to be expressed as

$$\delta = \frac{n \cdot e^2}{6\pi \cdot m \cdot c^2 \cdot a} \cdot \tfrac{1}{2}(W_+ + W_-) \tag{3}$$

where

$$W_+ = \frac{1}{[(1+r)^2 + z_+^2]^{\frac{1}{2}}} \cdot \left[K_+ + \frac{1 - r^2 - z_+^2}{(1-r)^2 + z_+^2} \cdot E_+ \right] \tag{4}$$

n = number of electrons involved in the current
e = unit charge of an electron
m = mass of an electron
c = velocity of light
a = radius of the ring
r and z = the cylindrical coordinates of the nucleus
    expressed in units of radius "a" and having
    an origin of the center of the ring
$z_+ = z + d/2$ and $z_- = z - d/2$
d = distance between the two loops
K and E = the complete elliptic integrals of the first kind and second kind,
    respectively, with a modulus, k,

$$k = \left[\frac{4r}{(1+r)^2 + z^2} \right]^{\frac{1}{2}}$$

Hence, given the position of the nucleus relative to the center of the ring, its chemical shift can be computed (having assumed a value for n, a, and d). A computer program was written for calculating chemical shifts due to the ring-current effect according to eqn. (3). The complete elliptic integrals of the first and second kind were expanded into convergent infinite series following published tables of integrals[35]. The cyclopentadienyl ring calculations assumed a ring with radius 1.21 Å and six electrons involved in the ring current. The distance between the loops above and below the ring plane was taken as 1.28 Å. Calculated differences between the indenyl and cyclopentadienyl compounds were obtained by considering a benzene ring with its center at

coordinates (2.42, 0, 0)*, having a radius of 1.39 Å, six electrons involved in the ring current, and the distance between the two loops was again taken as 1.28 Å. The anisotropy of the carbonyl group was considered by assuming the orientation of the ring plane perpendicular to the C–O bond, the radius of the rings as 1.0 Å, and the centers of the two loops as the carbon and oxygen atoms, respectively.

In consideration of the orientation of the indenyl group a potential well was proposed. The relative probability for each orientation was obtained from the potential according to the Boltzmann distribution factor assuming a temperature of 0°**. The chemical shift was calculated and multiplied by the weight in the corresponding orientation angles taken at 1° or 2° intervals. The potential well is considered to be a cosine curve. Two kinds of widths of the potential well were considered; that is, 72° and 360° wells. The minimum potential was assumed to arise when the orientation of the indenyl group was directly over the allyl group ($\theta = 0°$). The sum of the weighted chemical shifts for all angles divided by the sum of the weights gave the average chemical shift.

ACKNOWLEDGEMENTS

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* The coordinate may be changed when the benzene ring is not in the same plane as the cyclopentadienyl plane; *i.e.*, $\gamma \neq 180°$.

** The quantum mechanical solution for the probability gives nearly identical results with wells of the depths considered here[20].

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