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Preliminary communication

Organometallic conformational equilibria
XIII. Ring currents in the elucidation of organometallic stereochemistry*

J.W. FALLER and A. JAKUBOWSKI
Department of Chemistry, Yale University, New Haven, Connecticut 06520 (U.S.A.)

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A knowledge of the detailed stereochemistry of coordinated olefinic moieties is essential to the understanding of stereospecificity in certain organometallic reactions. Studies of temperature-dependent NMR spectra have been useful in the determination of mechanistic pathways; nevertheless, it has often been difficult to establish the configuration associated with a particular set of resonances. Studies of conformational equilibria in solution indicate that determination of the structure in the solid will not necessarily establish the predominant configuration in solution. In the solid, for example, certain allylpalladium complexes have different geometries for the allyl moiety depending upon the other ligands; yet, due to the facile equilibrium between the conformations in solution, only slight differences are noted in the percentages of each conformation in solution[1]. In using the nonequivalence of the 1- and 3-protons of π-indenyl ligands as a structural and mechanistic tool[2], we have noted extraordinarily large magnetic anisotropies associated with the indenyl ligand which appear to provide a generally useful technique for the determination of stereochemistry.

The possibility of different modes of binding of the allyl moiety in π-cyclopentadienylmolybdenumdicarbonyl-π-allyl was originally noted by King[3]. Davison and Rode[4] demonstrated that a rapid conformational equilibrium did indeed exist in this compound and subsequent work[5] 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[6—9]; nevertheless, convincing evidence for assigning given configurations has been lacking. The conformations which appear most likely to be involved differ by a rotation about the metal-allyl axis. The recent X-ray structural analysis of π-cyclopentadienylmolybdenumdicarbonyl-π-benzyl which contains a π-allylic—Mo linkage, further substantiates the suggested geometry[10]. Comparison of the intensities of infrared 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 chemical shifts, however, shows large shifts attributable to the magnetic anisotropy of the indenyl ring

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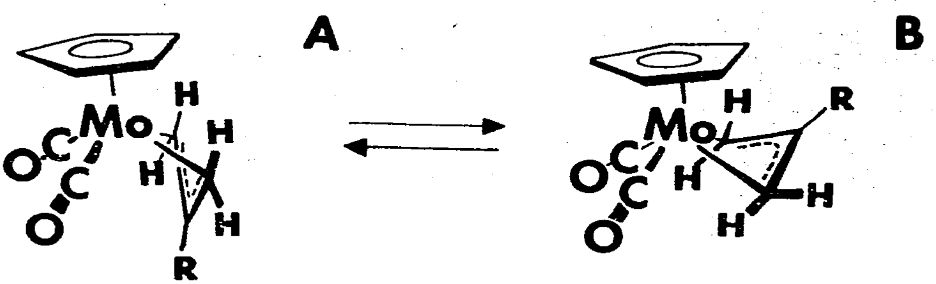
*For part XII see ref. 2.

TABLE 1

NMR AND INFRARED DATA FOR SOME π-ALLYL COMPLEXES

R		δ(R)[a]		δ_{syn}[a]		δ_{anti}[a]		ν(CO)[b]	B[c] (%)
		C_5H_5	C_9H_7	C_5H_5	C_9H_7	C_5H_5	C_9H_7	C_9H_7	
H	A	3.61	3.37	2.77	3.60	1.64	−0.68	1971, 1902	33
	B	3.61	0.15	2.70	2.39	1.02	1.15	1963, 1887	
Me	A	1.96	1.63	2.91	3.68	1.79	−0.58	1965, 1894	< 1
Cl	A	–	–	3.30	4.02	2.02	−0.39	1979, 1914	< 1
Br	A	–	–	3.25	3.89	2.04	−0.35	1980, 1916	< 2
	B	–	–	–	–	–	–	1967, 1898[c]	
π-benzyl	A	6.30[d,e]	2.13[d]	2.80[e]	4.14	1.80[e]	−0.21	1960, 1887	< 1

[a] Chemical shifts are given in ppm downfield from TMS at 100 MHz in benzene at 5°. [b] Carbonyl stretching frequencies are given in cm^{-1} as observed for cyclohexane solutions. [c] The percentages of isomers are given for benzene solutions at 5° and were determined by NMR. The isomer ratio is dependent on solvent, such that B is usually more prevalent in cyclohexane than in benzene or chloroform. [d] The chemical shifts listed are for the α-proton of the 1,2,α-*trihapto* benzyl group. [e] In bromopentafluorobenzene at −30° [3].



(see Fig. 1). An upfield shift is expected for the protons which approach nearest the ring, *i.e.*, the *anti* protons of the allyl in A and the central proton (or R group) in B. Thus the upfield shift (δ_{anis} +1.32) of the *anti* resonances of the minor isomer of the allyl (R = H) establish it as A; whereas the upfield shift (δ_{anis} +3.46) of the central proton of the major isomer establish it as B★. The stereochemistry of analogous compounds may also be readily established by this method and comparison with the parent compound (see Table 1). The benzyl complex is particularly illustrative since the X-ray results indicate the solid state structure of the cyclopentadienyl complex to be A and one of the *anti* protons is shifted above TMS in the π-indenyl complex★★.

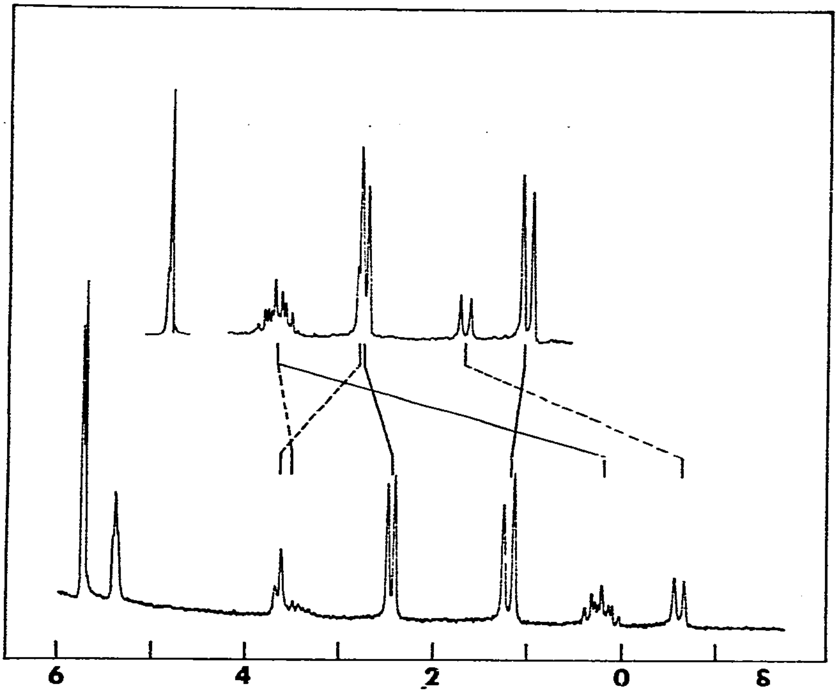
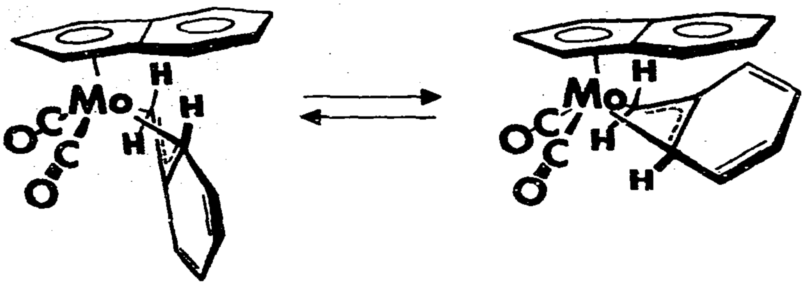


Fig. 1. 100 MHz proton magnetic resonance spectra of π-$C_5H_5Mo(CO)_2$–π-allyl (upper trace) and π-$C_9H_7Mo(CO)_2$–π-allyl (lower trace) in benzene at 5°.

★It should be noted that it is possible to have protons oriented such that significant average deshielding is observed; e.g. δ_{anis} = −0.83 ppm for the *syn* protons.

★★Determination of conformational interchange barriers indicate that equilibration of these conformers will be slow at low temperatures; hence, dissolving the solid complexes at low temperatures should assure determination of the same conformation as found in the solid.



Estimation of the magnitude of the magnetic anisotropy to be expected has been carried out anticipating the effect of a relatively low barrier to rotation about the molybdenum–indenyl axis[11]. Within the limits of the Johnson–Bovey model[12,13], the extraordinary magnitude of the shifts requires that a conformation is preferred in which the allyl group is positioned below the benzene ring of the indenyl ligand. The "ring current" model may be incapable of accounting for the magnitude of some of the shifts for reasonable choices of interatomic distances and well depths for the hindered rotation; hence, other sources may be responsible in part for the large magnetic anisotropy associated with the indenyl ligand. Details of these calculations will be published separately. Regardless of the specific origin of these large shifts, they empirically provide a method for assigning stereochemistry, which should prove useful for a variety of cyclopentadienyl complexes.

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