rough independent check on the measured value. It may not be fortuitous that the poorest agreement between observed and calculated $\mathcal{E}^\circ$ values obtains in just those cases where there is reason to believe the experimental data may not be reliable. In fact, with the exception of the aquo couples and the $Fe(CN)_6{}^{4-,3-}$ and $Fe(phen)_3{}^{2+,3+}$ couples, considerable uncertainty is associated with the reported $\mathcal{E}^\circ$ values. In many cases appropriate extrapolations that are necessary to anchor the $\mathcal{E}^\circ$ value on the conventional hypothetical ideal 1 m standard state have not been carried out. In this connection it is the opinion of the author that the results obtained here indicate that a reinvestigation of some of the couples whose $\mathcal{E}^\circ$ values have been reported is in order.

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Steric Effects in Organometallic Conformational Equilibria. I. Allylic Complexes of Molybdenum[1]

Sir:

The presence of four carbonyl stretching bands in the infrared spectrum of π-$C_5H_5Mo(CO)_2$-π-C_3H_4R (R = H or CH_3) suggests the existence of two different structures in solution.[2] Both the infrared and temperature-dependent nmr spectra of this compound have been rationalized by a conformational equilibrium between IA and IB[3] (see Figure 1). Although an analogous equilibrium would be expected for the methallyl complex, the novel effect of substitution upon the equilibrium allows one to deduce which of the conformers predominate.

At low temperature the proton nmr of I (see Figure 2) exhibits two π-cyclopentadienyl resonances and two superimposed AM_2X_2 spectra corresponding to the two conformations. As the temperature is raised, the corresponding peaks in the two isomers broaden and coalesce to a limiting high-temperature spectrum of resonances which are approximately weighted averages of those at low temperature. Over the temperature range observed there is no averaging of the *syn* and *anti* protons; this eliminates possible mechanisms for conformer interconversion which require *syn–anti* proton exchange[4-6] and suggests a mechanism equivalent to rotation of the planar π-allyl moiety about a molybdenum–allyl axis.[7]

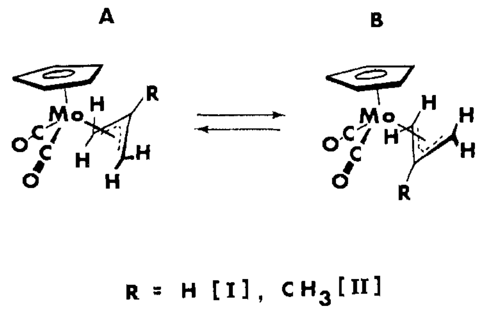

Figure 1.—Probable conformations of π-$C_5H_5Mo(CO)_2$-π-C_3H_4R.

The infrared spectrum in pentane shows two intense carbonyl bands at 1970 and 1902 cm^{-1}, and at low temperature the nmr spectrum apparently indicates that there is only one isomer of the π-methallyl derivative (II). The temperature dependence of the nmr spectrum, however, suggests a configurational equilibrium completely analogous to that of the π-allyl complex. The low concentration of the minor component and the presence of hydrocarbon impurities makes it difficult, but the resonances can be located at high spectrometric gain.[8,9] A comparison of the low-temperature proton resonances in compounds I and II (see Table I) results in the interesting conclusion that the structure corresponding to the minor constituent in I has become the major constituent in II. This unexpected reversal of concentrations in the equilibrium upon replacement of a hydrogen atom by a methyl group may be rationalized on the basis of steric factors. Examination of molecular models[10] based on the X-ray structural parameters of $(\pi$-$C_5H_5Mo(CO)_3)_2$[11] and $(\pi$-$C_3H_4RPdCl)_2$[12] indicates that the interactions between the ring hydrogen atoms and the two *anti* hydrogen atoms in conformer IB are greater than those with the hydrogen atom on the central carbon in conformer IA. In the methallyl complex the nonbonded interactions between the ring hydrogens and the methyl group in IIA are much greater than with the *anti* hydrogens in IIB, thus destabilizing IIA relative to IIB. Hence, it is concluded that two

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[1] These complexes may be classified as stereochemically nonrigid organometallic compounds. See, for example, W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

[2] R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

[3] A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

[4] F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **6**, 179 (1967).

[5] K. Vrieze, C. Maclean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim.*, **85**, 1077 (1966).

[6] J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc., Sect. A*, 423 (1967).

[7] The mechanism may perhaps be better described as a pseudo-rotation, such as that found in five-coordinate phosphorus species. The elucidation of this point is being pursued.

[8] Confirmation of the location of the *anti*-proton resonance of the minor component of II was provided by a double irradiation experiment. At 8° the region from 600 to 640 Hz upfield from benzene was irradiated while observing the major-component *anti*-proton resonance at 558 Hz. Assuming configurational interconversion occurs at a faster rate than spin-lattice relaxation of the *anti* protons, irradiation at the resonance position of the *anti* protons of the minor component should result in reduced intensity of the analogous resonance of the other component due to transfer of nuclear-spin polarization.[9] Irradiation between 620 and 622 Hz resulted in a minimum in the intensity of the resonance at 558 Hz. A similar experiment confirmed the location of the methyl resonance of the minor component of II.

[9] R. A. Hoffman and S. Forsen, *Progr. Nucl. Magnetic Resonance Spectry.*, **1**, 15 (1966).

[10] The conformations shown in Figure 1 are distorted for clarity. If there were no steric interactions to distort the bond angles, the model compounds suggest that the C–C–C plane of the allyl in B should be nearly perpendicular (~77°) to the plane of the cyclopentadienyl ring; whereas in A the dihedral angle would be about 33°.

[11] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

[12] A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).

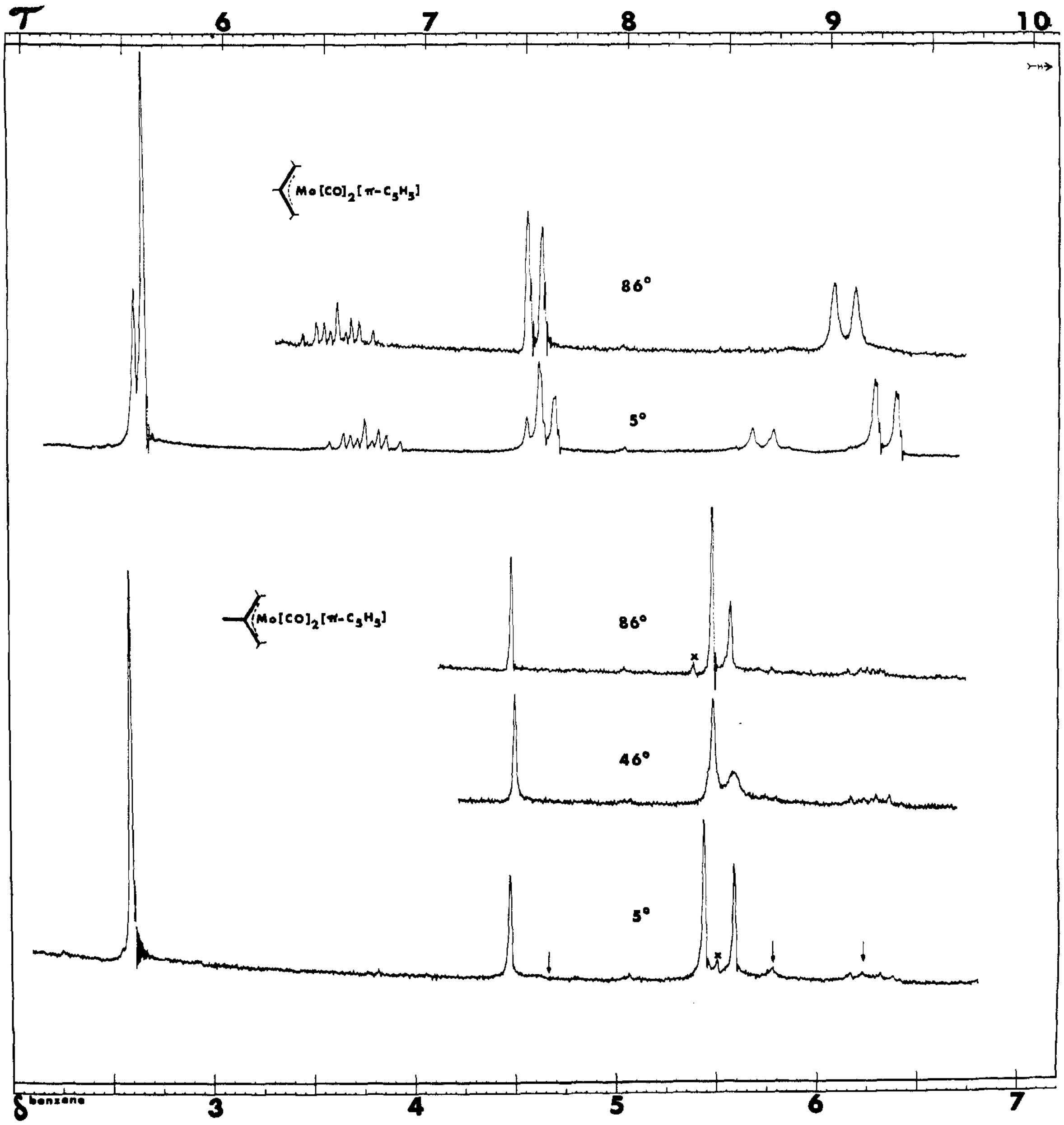

Figure 2.—The temperature dependence of the nmr spectra of π-$C_5H_5Mo(CO)_2$-π-C_3H_5 and π-$C_5H_5Mo(CO)_2$-π-C_4H_7. The spectra were recorded at 100 MHz on a Varian HA-100 spectrometer operated in the frequency-sweep mode.

TABLE I

PROTON CHEMICAL SHIFTS AT 100 MHz IN ALLYLIC MOLYBDENUM COMPOUNDS (IN Hz UPFIELD FROM BENZENE)

	I, 3:1[a]			II, 1:16[a]		
	Major (5°)	Minor (5°)	Average (86°)	Major (−8°)	Minor (−9°)	Average (80°)
π-C_5H_5	266	262	251	264	~264	247
syn	467	460	462	446	461	447
anti	635	573	615	558	621	556
R	376	376	363	541	578	546

[a] Population ratio for the higher field *anti*-proton resonance to the lower field *anti*-proton resonance.

opposing steric factors govern the magnitude of the equilibrium constant: (1) ring hydrogen–*anti* hydrogen interaction; (2) ring hydrogen–R interaction.

Palladium–π-allylic complexes offer substance to the conclusion that steric factors rather than electronic factors principally account for the alteration in the population ratio upon replacement of the hydrogen atom with a methyl group. For bis(π-allyl)palladium at −20° in $CDCl_3$ the relative population of the two configurations[6] is 3:1; in $CDCl_3$ at 8° we have found that the relative population for the bis-π-methallyl compound is 2.1:1. In both compounds the higher field *anti*-proton resonance and the lower field *syn* resonance correspond to the major component; hence, for both the π-methallyl and the allyl palladium complexes, the same isomeric form is in higher concentration.[13]

(13) In benzene, bis(π-allyl)palladium[6] and bis(π-methallyl)palladium exhibit, respectively, resonances at the following τ values: major *syn*, 5.95, 6.08; minor *syn*, 6.15, 6.26; major *anti*, 7.62, 7.54; minor *anti*, 7.57, 7.48. This further suggests that one should only expect small changes in chemical shift with substitution.

The chemical shifts of the resonances are quite sensitive to solvent properties.[14] Hence one notes that the positions of the resonances at high temperatures are not exactly those of the weighted averages of the low-temperature resonances. This limits the accuracy with which one can calculate exchange rates from the line shapes; however, the changes are not so severe that one cannot obtain approximate activation energies using the Kubo–Sack matrix method for line-shape analysis.[15] For complex I the activation parameters for the rate of conversion of one conformation to the other were determined by matching the experimental and computed line shapes of the cyclopentadienyl resonances over a temperature range of −5.5 to +9.5° for seven points and gave a value of E_a = 12.3 ± 1.2 kcal/mole and log A = 10.6 ± 1.0. The methyl resonance line shape for the methallyl complex (II) was used to determine both the relative populations and the rates. A least-squares fit of five points[16–19] between 13.5 and 54.5° gave E_a = 16.8 ± 0.4 kcal/mole and log A = 14.5 ± 0.3. These activation parameters for configurational interchange without *syn–anti* exchange may be compared with activation energies of 9 to approximately 20 kcal/mole for *syn–anti* exchange through a σ-bonded intermediate[20] for compounds of the form $L_2Cl_2Rh(\pi\text{-}C_4H_7)$.[21,22] We therefore conclude that opposing steric factors require that A predominate in the π-allyl complex and conformer B predominate in the π-methallyl complex. The apparently greater activation energy for the π-methallyl complex indicates further steric interactions in the transition state during interconversion of conformers.[23–25]

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[14] The chemical shift of the *anti*-proton resonance for II is highly solvent dependent: in CS_2 the major *anti* resonance is 0.10 ppm downfield from the major methyl resonance, and in C_2Cl_4 it is 0.03 ppm downfield at low temperature and merges into the methyl resonance as the temperature is raised.

[15] R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957); R. A. Sack, *Mol. Phys.*, **1**, 163 (1958). We are indebted to Professor Martin Saunders for supplying a computer program which carried out the matrix manipulations.

[16] Use of the *anti*-proton resonances was less reliable owing to impurity interference,[17] but it gave E_a = 14.5 ± 1.8 kcal/mole and log A = 12.5 ± 1.3 and a population ratio of 14.5:1 (compared to 16:1 from the methyl resonance). The solvent dependence of the chemical shifts in these compounds makes all of the activation energy calculations somewhat less reliable than normal; nevertheless, it is felt that the difference between the π-allyl and the π-methallyl compounds is significant. We have assumed that the equilibrium constant for the interconversion of conformers is independent of temperature. This should be valid on the basis of the low-temperature behavior of both the palladium and molybdenum complexes and has also been noted in nickel–allyl complexes.[18] Considering the uncertainties and magnitudes which one expects in these E_a calculations, the values of ΔH (assuming $\Delta S \sim 0$) of 0.6 and 1.6–1.8 kcal/mole, respectively, for the allyl- and methallyl-molybdenum complexes suggest that the energy profile is effectively symmetric, such that E_a was obtained from the observed rates.

[17] Difficulty in obtaining π-allylic complexes free from impurities has been noted elsewhere.[19]

[18] H. Boennemann, B. Bogdanovic, and G. Wilke, *Angew. Chem.*, **79**, 817 (1967).

[19] C. A. Reilly and H. Thyret, *J. Amer. Chem. Soc.*, **89**, 5144 (1967).

[20] K. Vrieze and H. C. Volger, *J. Organometal. Chem.* (Amsterdam), **9**, 537 (1967).

[21] We have noted in experiments similar to those of Becconsall and O'Brien[22] that in bis(π-methallyl)palladium the temperature dependence is due to both *syn–anti* and conformational interchanges and that the line shapes could not be matched by considering the effect of a σ-bonded intermediate mechanism alone. The decomposition occurring in the palladium system makes any definitive conclusions difficult.

[22] J. K. Becconsall and S. O'Brien, *J. Organometal. Chem.* (Amsterdam), **9**, 27 (1967).

[23] The methallyl-molybdenum complex was a yellow solid which melted to an oil above room temperature and was prepared by a method similar to that for the allyl complex.[24]

[24] M. Green and M. Cousins, *J. Chem. Soc., Sect. A*, 889 (1963).

[25] We are indebted to the Climax Molybdenum Corp. for a gift of molybdenum carbonyl, the Petroleum Research Fund for financial support, and the National Science Foundation for the departmental grant which supplied the HA-100.

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New Conformers of Tris(ethylenediamine)chromium(III)

Sir:

In the conformational analysis of metal chelates, the relatively simple tris(ethylenediamine) complexes have received considerable attention.[1] In these complexes there are two ways the carbon–carbon bond of the ethylenediamine (en) ring can bend to achieve the unstrained *gauche* conformation. In the first of these the carbon–carbon bond is nearly parallel to the threefold axis of the metal complex, and in the second it forms an obtuse angle with this axis. For a Λ configuration[2] about the metal, these ring conformers are designated δ and λ, respectively. The Λ absolute configuration is defined by assigning it to that isomer of the complex which, when viewed down the *threefold axis*, forms a left-handed propeller. The mirror-image isomer is designated Δ. This allows the eight possible isomers: Λδδδ, Λδδλ, Λδλλ, Λλλλ, Δλλλ, Δλλδ, Δλδδ, Δδδδ. The last four are mirror images of the first four, in sequence, and the members of each stereoisomeric pair, of course, have identical conformational stabilities. For this reason only the first set of four conformers will be discussed in the following comparison of stabilities.

Corey and Bailar[3] calculated the relative energies of the Λδδδ and Λλλλ conformations of $[Co(en)_3]^{3+}$ (designated by them as kkk and k′k′k′, respectively). These calculations were based on a comparison of the nonbonded interactions in the ring systems and predicted the δδδ form to be 1.8 kcal/mole lower in energy than the λλλ form. X-Ray diffraction studies of several compounds (Table I) have supported this assignment since only the δδδ conformation was found. The compounds studied included only Co(III) and Ni(II) salts. However, ter Berg[4] has shown that the salts $[M(en)_3]Cl_3 \cdot 3H_2O$ (M =

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[1] See, for example, R. D. Gillard and H. M. Irving, *Chem. Rev.*, **65**, 603 (1965); J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, **9**, 185 (1966); A. M. Sargeson, "Transition Metal Chemistry," Vol. 3, Marcel Dekker, Inc., New York, N. Y., 1966, p 303.

[2] The recent IUPAC proposal for nomenclature is used here.

[3] E. J Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[4] J. ter Berg, *Strukturbericht*, **7**, 235 (1939).