Organometallic Conformational Equilibria. IV. Isomerism and Stereochemical Nonrigidity in Cyclopentadienylmolybdenum Complexes[1]

Sir:

In an effort to understand the mechanisms of isomer interconversion in π-cyclopentadienyldicarbonylmolybdenum π-allyl,[2] we undertook an investigation of stereochemical nonrigidity[3] in compounds of the type π-$C_5H_5Mo(CO)_2LR$. King and Pannell's recent report[4] of an inability to distinguish between the isomers of these complexes prompts us to report our preliminary results.

Monosubstitution products of π-cyclopentadienyldicarbonylmolybdenum alkyls can exist in two isomeric forms (see Figure 1), and both forms are usually present in solution. We have been able to distinguish these isomers and demonstrate that they undergo more or less rapid intramolecular interconversion depending upon the nature of the substituents.

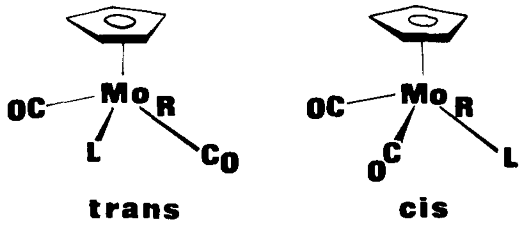

Figure 1. The isomers of a π-$C_5H_5Mo(CO)_2LR$ complex.

Although the infrared spectra of these compounds are very similar, one may readily distinguish the isomers by the pmr spectra. Empirically it is noted that, within a series containing different alkyl substituents, the cyclopentadienyl resonance of one of the isomers gives rise to a doublet ($J_p \sim 1.3$ Hz) due to a spin–spin coupling with the phosphorus atom, whereas the other isomer exhibits a singlet C_5H_5 resonance ($J_p < 0.2$ Hz).[5]

The key to correlating this splitting with the appropriate structure is the benzyl derivative. Even though rapidly rotating about the metal–carbon bond, the methylene protons of the benzyl group are nonequivalent when attached to an asymmetric moiety; hence, the methylene fragment in σ-benzyl-π-$C_5H_5Fe(CO)[P(C_6H_5)_3]$ gives rise to eight resonances, *i.e.*, the AB portion of an ABX spectrum (X = phosphorus, see Figure 2). Hence, in the spectrum of σ-benzyl-π-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$ (Figure 3), the methylene fragment of the isomer present to the extent of 13% gives rise to eight resonances and must therefore belong to the asymmetric *cis* isomer. In the more abundant *trans* isomer, in which the molybdenum-containing moiety has a plane of symmetry, the methylene protons are equivalent and give rise to only two resonances (due to phosphorus coupling). Since the cyclopentadienyl resonance of the major isomer is a doublet, and we have concluded that it is the *trans* isomer, this suggests that this type of splitting is generally diagnostic of the *trans* compound.[7] Thus we conclude for the triphenyl phosphite derivatives that the *trans* isomer predominates in the benzyl (87% *trans*) and methyl (61% *trans*) derivatives, whereas the *cis* isomer predominates in the hydride (0.4% *trans*).

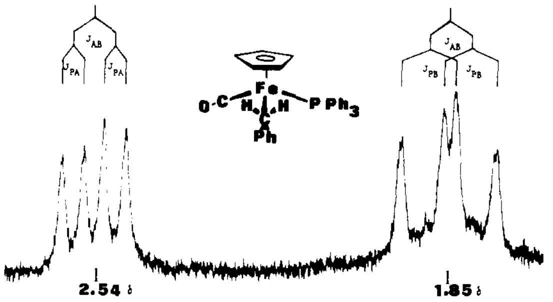

Figure 2. The pmr spectrum of the methylene fragment of σ-benzyl-π-$C_5H_5Fe(CO)P(C_6H_5)_3$ in chloroform-d_1.

Caution is warranted in the application of this criterion if only one isomer appears to be present, because in some cases the equilibria between the isomers is quite rapid and may lead to an averaged spectrum. The rate of isomer interconversion of the benzyl and methyl compounds increases at higher temperatures to a sufficient rate ($k > 100$ sec^{-1}) that an averaged spectrum is observed above 130°. The spectrum of the hydride, on the other hand, is averaged at room temperature and broadens at lower temperatures to the "static" spectrum at −80°. The spin coupling to the phosphorus atom persists in the averaged spectrum of these compounds;[9] consequently the interconversions must be intramolecular. Although the complexes are considered as derived from a seven-coordinate idealized structure, a rearrangement mechanism reminiscent of the pseudorotation mechanism[10,11]

---

[1] Part III: J. W. Faller, M. J. Incorvia, and M. E. Thomsen, *J. Am. Chem. Soc.*, **91**, 518 (1969).

[2] J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 7, 840 (1968).

[3] The term *stereochemically nonrigid* indicates that there is a rapid intramolecular rearrangement process which permutes the ligands among some (or all) of the various coordination positions. This terminology is discussed more completely elsewhere; *e.g.*, F. A. Cotton, J. W. Faller, and A. Musco, *J. Am. Chem. Soc.*, **90**, 1438 (1968); and E. L. Muetterties, *Inorg. Chem.*, 4, 769 (1965).

[4] R. B. King and K. H. Pannell, *ibid.*, 7, 2356 (1968).

[5] Although prepared in a different manner (irradiation of the R-substituted derivative in the presence of phosphite or preparation *via* the mercury derivative[6]), the physical and spectroscopic properties which we have determined generally agree well with those of King and Parnell except for the relative percentages of the isomers.

[6] Similar complexes have been prepared *via* a mercury intermediate by M. J. Mays and S. M. Pearson, *J. Chem. Soc.*, *A*, 2291 (1968).

[7] We believe that the presence or absence of splitting in the cyclopentadienyl resonance is the most characteristic feature of the physical measurements. Nevertheless, we have noted the following trends: the chemical shift of the cyclopentadienyl resonance of the *trans* isomer is usually upfield of the *cis* isomer; and the highest frequency carbonyl stretching mode in the infrared spectrum is more intense in the *cis* isomer, but less intense in the *trans* isomer. This difference in intensities has been noted and discussed by other workers, particularly with respect to halide derivatives.[6,8]

[8] A. R. Manning, *J. Chem. Soc.*, *A*, 651 (1968); 1984 (1967).

[9] The averaging is most impressive in the methyl derivative. The ambient temperature spectrum in toluene-d_8 exhibits the following resonances with the chemical shift, δ, and phosphorus coupling constant in parentheses: phenyl, ~7.2; *trans*-C_5H_5, 4.56 (1.3); *cis*-C_5H_5, 4.68 (< 0.1); *trans*-Me, 0.77 (2.6); and *cis*-Me, 0.74 (10.3). The resonances of the *cis* (39%) isomer and the *trans* (61%) isomer average to the following at 140°: phenyl, 7.2; C_5H_5, 4.81 (0.7); Me, 0.67 (5.6). There is some change in the chemical shifts with temperature, as expected, but the spin coupling averages exactly as calculated.

Our studies also indicate that bisphosphine hydrides, alkyls, and halides are also stereochemically nonrigid and often require lowering the temperature to "freeze out" the rearrangement processes.

[10] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[11] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

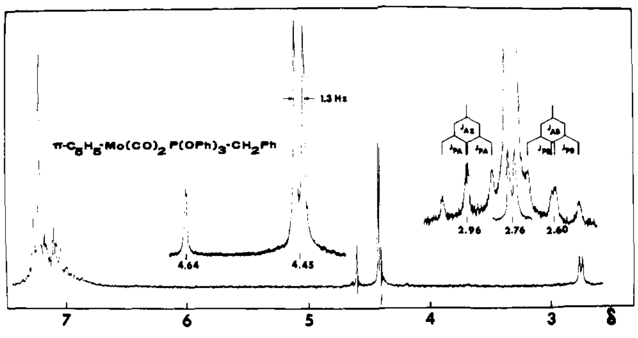

Figure 3. The pmr spectrum of σ-benzyl-π-$C_5H_5Mo(CO)_2$-$P(OC_6H_5)_3$ in chloroform-d_1 at ambient temperature.

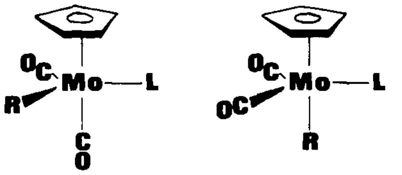

Figure 4. Two of several possible intermediates or transition states expected in the intramolecular rearrangement processes.

of five-coordinate complexes appears likely. Hence intermediates or transition states such as those indicated in Figure 4 might be anticipated.[12]

We are currently investigating the thermodynamics and kinetics of these complexes in order to determine the steric and electronic factors responsible for the stability of a given configuration, the barriers to interconversion, and the plausibility of suggested mechanism of ligand interchange. We tentatively assume that the lowest energy pathway of rearrangement would suggest an intermediate or transition state with the least bulky group in the "apical" position. Hence, in the hydride the lowest energy pathway would involve movement of a hydrogen atom to an apical position. In the alkyl complexes, placing either the carbonyl or the alkyl group in the apical position could result in a comparable situation energetically, and more than one pathway might be important.[14,15]

---

(12) The structures in Figure 4 are only meant to imply relative ligand orientation, not bond angles. These structures were suggested by the most stable conformations of seven-coordinate complexes[13] and the possibility of a rapid 3:4 = 3:3:1 = 3:4 conformational interconversion.

(13) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

(14) The benzyl and methyl derivatives exist in the *trans* form in the solid; hence, one can observe the kinetics of interconversion by measuring concentrations as a function of time at low temperature and nmr line-shape analysis at high temperatures. This allows very accurate determinations of barriers since one can measure rate constants over a range of 10^6 in rate constant and 150° in temperature.

(15) We wish to acknowledge the financial support of the Connecticut Research Commission and the Petroleum Research Fund administered by the American Chemical Society. We wish to thank the National Science Foundation for Grant GP-6938 which allowed the purchase of the Varian HA-100 spectrometer.

J. W. Faller, A. S. Anderson
Department of Chemistry, Yale University
New Haven, Connecticut 06511
Received December 26, 1968

Titanium(II) in the Fixation–Reduction of Molecular Nitrogen under Mild Conditions

Sir:

In previous communications[1-3] we have described the facile room-temperature, atmospheric pressure conversion of molecular nitrogen (N_2) to ammonia by means of an over-all catalytic, titanium-based process involving a fixation–reduction–protonation sequence. In the reaction, aerial N_2 can be utilized,[2] and the reduction can be effected by either chemical or electrolytic means.[3] The central role of a titanium(II) species had served from the outset as an ideological guide in the design of our experiments,[1,4,5] and the function of this unusual, lower valent titanium type has now been clarified by findings which include the first case of the detention and subsequent reductive conversion to ammonia of a given transition metal compound made directly by reaction with N_2 or by other means.[6]

In a typical experiment dicyclopentadienyltitanium ("titanocene") (1.50 g, 8.40 mmol), dissolved in 95 ml of anhydrous, oxygen-free benzene at 20–25°, was exposed with stirring to an atmosphere of N_2.[7] During the course of approximately 3 weeks, 7.56 mmol of the gas was absorbed, after which N_2 uptake ceased. Similar behavior was observed when a preparation of titanium(II) *n*-hexoxide (prepared by reaction of titanium(III) chloride, *n*-hexyl alcohol, and methyllithium in a 1:2:3 molar ratio)[5] was dissolved in benzene and exposed to an atmosphere of N_2. Significantly, titanium(II) alloxide and benzoxide, useful for achieving coupling of hydrocarbon units,[5] were ineffectual in fixing nitrogen, possibly because of stabilization due to internal coordination with titanium of the π electrons of the unsaturated ligands. The titanocene–N_2 reaction is reversible under the conditions described. Thus, in one run, the reaction was interrupted after 30% reaction by quickly flushing argon through the system; during 50 successive hr all of the chemically bound N_2 was released into the argon atmosphere, as indicated by the volume change.

Treatments of this titanium–nitrogen complex in benzene with excess sodium naphthalide (NaNp) and subsequent hydrolysis produced high yields of ammonia. Further, a solution of this complex in benzene showed an infrared absorption at *ca.* 1960 cm^{-1} which may be attributable to an N–N stretch and which disappeared after the solution was exposed overnight to an argon atmosphere. An osmometric molecular weight determination in benzene indicates that the nitrogen complex is dimeric.

In order to ascertain the stoichiometry of the over-all

---

(1) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967).

(2) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(3) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(4) E. E. van Tamelen and M. A. Schwartz, *ibid.*, **87**, 3277 (1965).

(5) For the role of titanium(II) species in the one-step coupling of alcohols to hydrocarbons, see E. E. van Tamelen, B. Åkermark, and K. B. Sharpless, *ibid.*, **91**, 1552 (1969).

(6) Previously, an order of stability sufficient to permit isolation of transition metal compounds with N_2 ligands apparently also precluded reduction or oxidation of the ligand: J. Chatt, R. C. Richards, J. E. Ferguson, and J. L. Love, *Chem. Commun.*, 1522 (1968).

(7) The use of titanocene for the *over-all* conversion of molecular nitrogen to ammonia was first described in a publication from this laboratory.[1] The metallocene was prepared according to the directions of G. W. Watt, L. J. Baye, and F. O. Drummond, *J. Am. Chem. Soc.*, **88**, 1138 (1966).