Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

ORGANOMETALLIC CONFORMATIONAL EQUILIBRIA
V*. π-$C_5H_5Mo(H)(CO)_2(PPh_3)$

J.W. FALLER, A.S. ANDERSON and CHIN-CHUN CHEN
Department of Chemistry, Yale University, New Haven, Connecticut 06520 (U.S.A.)

(Received March 14th, 1969)

A 3:4 structure for π-$C_5H_5Mo(H)(CO)_2(PPh_3)$ with the cyclopentadienyl ring occupying three coordination positions above the molybdenum atom, and the hydrogen, phosphorus, and two carbonyl carbon atoms forming an approximate square below, permits *cis–trans* isomerism. As in π-$C_5H_5W(H)(^{13}CO)(CO)_2$ [1] and π-$C_5H_5Mo(H)(CO)_2[P(OPh)_3]$ [2], these isomers are in rapid equilibrium on the NMR time scale at room temperature, giving rise to an averaged PMR spectrum above 40°. In $CDCl_3$ resonances are observed at 2.65 (multiplet), 4.97 (doublet, $J(P) = 0.5$ Hz), and 15.60 (doublet, $J(P) = 48.6$ Hz) in the expected 15:5:1 ratio for the phenyl, cyclopentadienyl, and hydride protons. In contrast to π-$C_5H_5Mo(H)(CO)_2[P(OPh)_3]$, which is present in solution almost entirely as the *cis* conformer (99.6% *cis*), the triphenylphosphine derivative exists in solution with comparable amounts of each isomer. For this reason, the phosphine derivative is more amenable to NMR line shape analysis** and the calculation of rate constants for ligand interchange.

Upon lowering the temperature to −37° individual cyclopentadienyl and hydride resonances may be integrated, giving 40.0% *trans* and 60.0% *cis* isomer. Further lowering of the temperature does not greatly alter*** this "static" spectrum which exhibits the *cis* and *trans* cyclopentadienyl resonances at 4.80 τ ($J(P) < 0.3$ Hz) and 5.00 τ ($J = 1.0$ Hz) respectively. The hydride resonances of the *cis* (15.33 τ) and *trans* (16.14 τ) compounds average in the manner which requires the coupling constants to the phosphorus ligand, $|J(PH_{cis})| = 64.0$ Hz and $|J(PH_{trans})| = 21.4$ Hz, to have the same sign. Since these hydride coupling constants do not average exactly to the 48.6 Hz observed at +40.0°, either the equilibrium constant or the coupling constants must change with temperature. We have found that in most of these systems the coupling constants in the "static" compounds are neither temperature nor solvent sensitive. Furthermore, from spectra from −43° to −65° it was observed that the coupling constants remained the same, while the equilibrium constant ($K = [cis]/[trans]$) decreased as the temperature was lowered. As the

---

*For Part IV see ref.1.

**Line-shape analysis has been discussed in previous papers in this series. A comprehensive discussion has been published by Johnson[3].

***Small changes in line widths due to residual slow exchange effects and small changes in relative intensities due to temperature dependence of the equilibrium constant are observed.

temperature was raised to +72.0°, where decomposition to red $[\pi\text{-}C_5H_5Mo(CO)_2(PPh_3)]_2$ is extremely rapid, the increasing value of the equilibrium constant could be calculated from the averaged ^{31}P-hydride coupling constant. From the slope of a plot of log K *vs* $1/T$, the enthalpy of the *cis* isomer is calculated to be 295 ± 7 cal·mole^{-1} greater than that of the *trans* isomer.

PMR investigations of possible mechanisms for intramolecular ligand rearrangement between *cis* and *trans* conformers of the general formula $\pi\text{-}C_5H_5Mo(R)(CO)_2L$ (R is alkyl, aryl, halide, or hydride; L is a tertiary phosphine, phosphite, arsine or stibine) have been especially fruitful. The persistence of the phosphorus coupling in both the cyclopentadienyl and hydride resonances of the averaged spectra of $\pi\text{-}C_5H_5Mo(H)(CO)_2(PPh_3)$ and $\pi\text{-}C_5H_5Mo(H)(CO)_2[P(OPh)_3]$ indicates that the mechanism must be intramolecular (assuming that the carbonyls do not dissociate). No intermolecular exchange of CO in this process is strongly suggested by the retention of the ^{13}C coupling in the averaged hydride resonance of the more soluble $\pi\text{-}C_5H_5W(H)(^{13}CO)(CO)_2$ [1]. Since a dissociative mechanism within a solvent cage or other non-intermolecular dissociation–recombination mechanisms would also be consistent with the above observations, $\pi\text{-}C_5H_5Mo(CO)_2(PPh_3)(D)$ was prepared so that any kinetic isotope effect could be measured. Comparison of the cyclopentadienyl regions of the PMR spectra of the hydride and deuteride at −37° indicates that the exchange rate is almost the same for both compounds. Line-shape analysis yields $k_H/k_D = 1.06$ (estimated uncertainty ± 0.05); therefore, the molybdenum–hydrogen bond effectively retains the same character in the transition state. Hence, all mechanisms of ligand interchange involving dissociation of the hydrogen atom may be eliminated. Such information is consistent with a 3:3:1 transition state, in which the hydrogen atom probably would occupy the apical position.

A least squares analysis of the fit of the rate constants (15 points) to the Arrhenius equation gives an activation energy of 12.3 ± 0.1 kcal · mole^{-1} (log A = 12.4 ± 0.1) for *trans* to *cis* interconversion, and Ea = 12.0 ± 0.1 kcal · mole^{-1} (log A = 12.0 ± 0.1 kcal · mole^{-1}) for the reverse reaction. The parameters obtained for the Eyring equation are: $\Delta H^{\ddagger} = 11.8 \pm 0.03$ kcal · mole^{-1}, $\Delta S^{\ddagger} = -3.36 \pm 0.12$ eu *trans* → *cis*; $\Delta H^{\ddagger} = 11.5 \pm 0.03$ kcal · mole^{-1}, $\Delta S^{\ddagger} = -5.35 \pm 0.12$ eu *cis* → *trans*. At 25° for the reaction *trans* → *cis*, the thermodynamic quantities determined from the variation of the equilibrium constant are: $\Delta H = 295 \pm 7$ cal · mole^{-1} ($\Delta\Delta H^{\ddagger} = 0.3$ kcal · mole^{-1}); $\Delta F = -310 \pm 9$ cal · mole^{-1} ($\Delta\Delta F^{\ddagger} = -0.3$ kcal · mole^{-1}); and $\Delta S = 2.03 \pm 0.03$ eu ($\Delta\Delta S^{\ddagger} = 1.99$ eu)★.

In compounds such as $\pi\text{-}C_5H_5Mo(CH_3)(CO)_2[P(OPh)_3]$ where bulkier groups must be accommodated in crowded positions in the transition state, activation energies appear to be more than 5 kcal · mole^{-1} greater than those in the hydride complexes, $\pi\text{-}C_5H_5Mo(H)(CO)_2(PPh_3)$, $\pi\text{-}C_5H_5Mo(H)(CO)_2[P(OPh)_3]$ and $\pi\text{-}C_5H_5W(H)(CO)_2(^{13}CO)$. If one assumes that the hydride ligand occupies the apical position in the lowest energy transition state, contributions to the first order rate constant from interconversions through other transition states (as for example with carbonyl groups or phosphines in the apical position) would be negligible (< 0.1%) if the same difference of 5 kcal · mole^{-1} in activation energies were appropriate.

★The small standard deviations in these parameters are indicative of the precision which can be obtained with the Kubo–Sack matrix method of NMR line-shape analysis for rates, if a wide temperature range is available and chemical shifts are large. Nevertheless, precision is indicated and systematic errors undoubtedly give rise to poorer accuracy.

ACKNOWLEDGEMENT

We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Connecticut Research Commission (Grant RSA 68-5) for support of this work; and to the Climax Molybdenum Corporation for a gift of molybdenum carbonyl.

REFERENCES

1 J.W. Faller, A.S. Anderson and Chin-Chun Chen, *Chem. Commun.*, in press.
2 J.W. Faller and A.S. Anderson, *J. Amer. Chem. Soc.*, 91 (1969) in press.
3 C.S. Johnson, Jr., *Advances in Magnetic Resonance*, vol 1, Academic, New York, 1965.