

ment of the results yields $\Delta F(2) = 829 - 5.42T$, $\Delta F(3) = 1640 - 5.96T$, $\Delta F(4) = 1910 - 4.15T$, and the following percentages of tetrahedral form at 25°: 79% (2), 56% (3), 24% (4).

The results clearly show that the equilibrium position is dominated by the nature of R such that the planar form is detectable only when R = H. The implication is that a torsional twist induced by steric interaction in the *trans*-planar form destabilizes this configuration, as is believed to be the case for nickel complexes.¹⁻⁴ Although no truly quantitative comparisons can yet be made, it is clear that the barrier to distortion from planarity of nickel complexes is much greater than that for cobalt complexes containing the same ligand. Thus, for the *nickel* complexes 2, 3, and 4 no contact shifts are observable at 80° in chloroform ($K < 0.01$, $\Delta F > 3200$ cal./mole); for the complex with $R_\alpha = R_\gamma = R = \text{CH}_3$, $R_\beta = \text{H}$, very small contact shifts are observed,³ implying $K \sim 0.02$, $\Delta F \sim 2400$ cal./mole, whereas the cobalt complex is fully tetrahedral. While the greater relative stabilization of tetrahedral Co(II) might be anticipated from CFSE arguments, the present work demonstrates that this stereoisomeric form is not exclusively populated in cobalt complexes which, by virtue of their structural and steric features, are not constrained to be either tetrahedral or planar.¹⁰ A more detailed account of this work will be forthcoming.

Acknowledgment. This research was supported by the National Science Foundation under Grants GP-2840 and GP-4899.

(10) The only other example of this type appears to be bis(dipivaloylmethanato)cobalt(II), which is tetrahedral in the solid (F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962)) and apparently fully tetrahedral in benzene (F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964)). The nickel complex is planar in both phases.

(11) N.S.F. Predoctoral Fellow, 1962-1966.

(12) Alfred P. Sloan Foundation Fellow.

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Received October 4, 1965

Reaction of Triphenylphosphine with Methylmanganese Pentacarbonyl. Structure and Stoichiometry

Sir:

Although the reactions of various amines,¹ phosphines,^{2,3} and arsines³ with $\text{CH}_3\text{Mn}(\text{CO})_5$ have been reported, the structures and stoichiometry of the products are not well known in each case. Certain of our preliminary results concerned with these aspects have already been mentioned.² We now wish to report some important observations on the reaction of triphenylphosphine with $\text{CH}_3\text{Mn}(\text{CO})_5$.

When triphenylphosphine reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$ in a wide selection of organic solvents for 12-24 hr. at 5-10°, a yellow solid (I) was obtained by blowing the solution down to a small volume with a stream of dry nitrogen. These solutions were not allowed to warm

(1) K. A. Keblyns and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(2) R. J. Mawby, F. Basolo, and R. G. Pearson, *ibid.*, **86**, 5043 (1964).

(3) W. D. Bannister, M. Green, and R. N. Hazeldine, *Chem. Commun.* (London), **1**, 55, 1965.

before the solid was filtered and freed of solvent. An infrared spectrum of I in hexane contained three terminal CO stretching frequencies at 2066 (w), 1995 (m), and 1959 (s) cm^{-1} , as well as an acetyl CO stretching frequency near 1631 (w) cm^{-1} . The spectrum was identical with that seen when the reaction itself was followed by infrared at temperatures near 5°. The number of carbonyl transitions and their relative intensities were as expected for *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ with localized C_{4v} symmetry for the metallo-carbonyl groups. Unfortunately, infrared spectral studies do not permit an unequivocal determination of isomeric purity, *i.e.*, *cis* or *trans*, and cannot provide an accurate measure of extent of carbonylation or decarbonylation. Equally misleading are carbon-hydrogen analyses which are not very different for a triphenylphosphine-substituted methyl or acetyl derivative. By contrast, proton magnetic resonance is especially enlightening in both regards. A p.m.r. spectrum of I in benzene taken immediately after mixing revealed two acetyl methyl proton resonances at 161 and 145 c.p.s. relative to tetramethylsilane. These peaks could not be due to $\text{CH}_3\text{COMn}(\text{CO})_5$ or $\text{CH}_3\text{Mn}(\text{CO})_5$, which gave sharp singlets at 136 and -13 c.p.s., respectively. The ratio of the peak heights showed the peak at 145 c.p.s. to be approximately four times that at 161 c.p.s. We believe that these peaks correspond to *trans*- and *cis*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$, respectively, since the infrared spectra suggest the predominance of a *trans* complex. After 1 hr. at room temperature, during which the relative intensities of these two peaks had changed, an equilibrium mixture containing approximately 30% *cis* and 70% *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ was obtained. Some decarbonylation also occurred during this period (see below).

When the reaction of triphenylphosphine with $\text{CH}_3\text{Mn}(\text{CO})_5$ was carried out at room temperature in a closed system, thus preventing extensive decarbonylation of the phosphine-substituted products, the infrared spectrum of the reaction mixture (II) was similar to that seen at the lower temperature, only it was slightly less sharp in the metallo-carbonyl stretching region. The p.m.r. spectrum of such a sample prepared in a closed tube again indicated that an equilibrium mixture containing approximately 70% of the *trans* acetyl species was obtained at room temperature compared to nearly 80% *trans* at 5°. If this same reaction proceeded at room temperature in an open system, decarbonylation occurred and striking changes took place in the infrared spectrum in the metallo-carbonyl stretching region (see below). Other evidences for decarbonylation included diminishment of the intensity of the acetyl stretching mode and appearance of a new proton resonance, indicating formation of *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$.

The formation of pure *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ (III) was easily achieved by refluxing a benzene solution of equimolar quantities of $\text{CH}_3\text{Mn}(\text{CO})_5$ and triphenylphosphine for several hours. Recrystallization from ethanol-chloroform yielded gold crystals, m.p. 109.5-111.5°, yield 48%. *Anal.* Calcd.: C, 62.17; H, 4.08. Found: C, 62.17; 61.76; H, 3.90, 4.02. The infrared spectrum of III in hexane contained terminal CO stretching bands at 2055 (m), 1983 (m), 1968 (s), and 1939 (m) cm^{-1} and was consistent

with predictions for a *cis*-disubstituted octahedral tetracarbonyl complex. This infrared spectrum of III was invariant with time, whereas spectra of the isolated acetyl derivatives I or II varied rapidly with time as decarbonylation occurred. The proton resonance of the methyl group of III appears as two peaks of equal intensity at -5 and -13 c.p.s. in benzene. This splitting may arise from spin-spin interaction with the phosphorus-31 nuclei. Although manganese-55 ($I = 5/2$) can theoretically cause spin-spin splitting in $\text{CH}_3\text{Mn}(\text{CO})_5$ and in III, it appears not to do so in either case.

Further evidence for the equilibrium nature of this reaction was provided by two simple experiments. First, when carbon monoxide gas was bubbled into a benzene solution of III for 12 hr. at room temperature, nearly all of III was carbonylated. The p.m.r. spectrum of the resulting solution was identical with that obtained in the closed-tube reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with triphenylphosphine. That is, an equilibrium ratio of approximately 70% *trans*- and 30% *cis*-

$\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ was obtained (*cf.* ref. 2). Second, when a reaction mixture in a closed tube which had reached equilibrium at room temperature was heated to 45° for several hours, some of III was formed and the concentrations of each of the acyl isomers decreased, although there was little change in their relative concentrations.

Calderazzo⁴ has indicated that he has also observed the formation of two acyl isomers in this system, although he apparently did not specify assignments for the acyl proton resonances.

Other studies of this type in these laboratories have shown that triphenylarsine gave almost exclusively *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3$, whereas certain amines appeared to form exclusively *cis* derivatives.

(4) F. Calderazzo, private communication.

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Book Reviews

Thermal Methods of Analysis. Volume XIX. Chemical Analysis. A Series of Monographs on Analytical Chemistry and its Applications. By WESLEY WM. WENDLANDT, Department of Chemistry, Texas Technological College, Lubbock, Texas. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. x + 424 pp. 15.5 × 23.5 cm. \$16.50.

The term "thermal methods of analysis" is defined by Professor Wendlandt to mean those techniques in which some physical parameter of a system is measured as a function of temperature, that property changing as a function of temperature so as to yield useful information concerning the chemical system. These techniques include the relatively long-known thermogravimetry and differential thermal analysis as well as the more recently developed methods of effluent gas analysis, pyrolysis, dynamic reflectance spectroscopy, thermodilatometric analysis, and thermoluminescence. Although there have been a few books dealing with some of the individual thermoanalytical techniques, such as Duval's "Inorganic Thermogravimetric Analysis" and Smothers and Chiang's "Differential Thermal Analysis: Theory and Practice," this excellent book represents the first publication of a monograph dealing with the field as a whole and fills a long-felt need. Professor Wendlandt presents a critical review rather than a comprehensive survey of the literature of each thermal method. He wisely points out not only the advantages of each technique, but, just as importantly, discusses their limitations. The rapid growth in recent years in the use of these thermal methods of analysis has been stimulated by the increasing

availability of commercial instruments designed to make these measurements. An especially valuable part of this book is the well-presented discussion and evaluation of all the apparatus commercially available at the time of publication.

After a general introduction to thermal methods of analysis in Chapter I, there follow three chapters dealing with thermogravimetry. Chapter II presents a discussion of the parameters, sources of error, and limitations of thermogravimetry; Chapter III is a review of both commercial and noncommercial instruments that have been developed; and Chapter IV is a discussion of the analytical applications of this technique. There are then three chapters devoted to differential thermal analysis, arranged in the same order as those about thermogravimetry. Chapter VIII is concerned with thermometric titrimetry, IX with pyrolytic techniques, X with dynamic reflectance spectroscopy, XI with thermal analysis, and XII with miscellaneous thermal methods which include thermoluminescence, oxylluminescence, dilatometry, electrical conductivity, and high temperature methods applied to infrared spectroscopy and X-ray diffraction.

This book is Volume 19 in Interscience's "Chemical Analysis Series" edited by P. J. Elving and I. M. Kolthoff. It is highly recommended not only to the analytical chemist but to any scientist who is using or contemplating using thermoanalytical techniques.

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