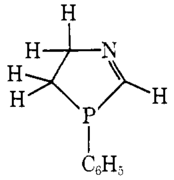
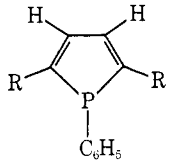
plexes.[5,6] However, the linear hybridizations of both the carbon and nitrogen atoms of the isocyanide group direct the lone pair on the isocyanide carbon atom so that it cannot coordinate with the same metal atom as the lone pair on the phosphorus or arsenic atom. This prevents the compounds $(C_6H_5)_2ECH_2CH_2NC$ from acting as bidentate chelating ligands. Accordingly the reaction between the norbornadiene complex $C_7H_8Cr(CO)_4$ and either $(C_6H_5)_2ECH_2CH_2NC$ derivative (E = P or As) in benzene at room temperature did *not* give monometallic $[(C_6H_5)_2ECH_2CH_2NC]Cr(CO)_4$ but instead gave good yields of yellow cyclohexane–insoluble diethyl ether soluble solids of approximate compositions $[(C_6H_5)_2ECH_2CH_2NC]_4Cr_3(CO)_{12}$ (E = P or As).[7] The infrared spectra of these compounds exhibited the expected[8] ν_{CO} frequencies for a *cis*-$L_2Cr(CO)_4$ derivative indicating that the stereochemistry of the nor-$C_7H_8Cr(CO)_4$ had been retained in this reaction. We tentatively formulate the $[(C_6H_5)_2ECH_2CH_2NC]_4Cr_3(CO)_{12}$ derivatives with *cis*-$Cr(CO)_4$ groups bridged by $(C_6H_5)_2ECH_2CH_2NC$ ligands with additional monodentate $(C_6H_5)_2ECH_2CH_2NC$ ligands as end groups.

The reaction of phenylphosphine with excess vinyl isocyanide in boiling tetrahydrofuran[9] in the presence of ~15% potassium *tert*-butoxide catalyst did *not* give the expected phosphine–diisocyanide $C_6H_5P(CH_2CH_2NC)_2$. Instead a very pale yellow air-sensitive viscous liquid, bp 64° (0.07 mm), of composition $C_9H_{10}NP$ was obtained in ~90% yield (*Anal.* Calcd for $C_9H_{10}NP$: C, 66.4; N, 6.1; N, 8.6; P, 19.0; mol wt, 163. Found: C, 66.3; H, 6.0; N, 8.5; P, 19.0; mol wt, 186 (osmometer in benzene); 163 (mass spec)). The infrared spectrum of $C_9H_{10}NP$ showed the absence of any ν_{CN} frequency around 2100 cm^{-1} that could be attributed to an isocyanide group. This indicates that the isocyanide group was destroyed in the reaction. The proton nmr spectrum of $C_9H_{10}NP$ ($CDCl_3$ solution) exhibited olefinic (τ 1.73 (doublet of triplets, J_1 = 56 Hz, J_2 = 2 Hz)), aromatic (τ 2.78 (unsymmetrical multiplet)), and two methylene resonances (multiplets at τ 5.8 and 8.1) of relative intensities 1:5:2:2. On this basis we formulate $C_9H_{10}NP$ as 4,5-dihydro-1-phenyl-3-azaphosphole (I). As far as we can ascertain,[10] this is the first simple derivative of the 3-azaphosphole system that has been prepared. However, somewhat similar phospholes of the type II have been previously prepared[11] by an analogous base-catalyzed addition of phenylphosphine to the 1,3-diynes RC≡C—C≡CR (R = CH_3, C_6H_5, etc.),


I


II

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(5) For a review of metal isocyanide complexes see L. Malatesta, *Progr. Inorg. Chem.*, 1, 283 (1959).

(6) For a review of metal complexes of tertiary phosphines and arsines see G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).

(7) These formulas were established by analyses for at least five elements and molecular weight determinations in benzene solution with a vapor pressure osmometer.

(8) F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964).

(9) This reaction failed to give any product when carried out in benzene rather than tetrahydrofuran solution under otherwise the same conditions.

(10) The 3-azaphosphole ring system is not listed in the Second Edition of the Ring Index or its first three supplements.

(11) G. Märkl and P. Potthast, *Angew. Chem., Int. Ed. Engl.*, 6, 86 (1967).

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Book Reviews

Markov Chains and Monte Carlo Calculations in Polymer Science. Edited by GEORGE G. LOWRY, Department of Chemistry, Western Michigan University, Kalamazoo, Mich. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1970. xi + 329 pp. 16 × 23.5 cm. $19.75.

According to the preface, this book has been "... written primarily for the polymer chemist who is not an expert in mathematical theories but who wants to be conversant with the topics treated." It is this reviewer's opinion that the editor and other contributors have been successful in producing a book useful to such a reader; they have presented good introductory accounts of the two mathematical methods cited and have clearly discussed their application to a variety of problems in polymer science.

In the first of these methods, Markoffian chain models, the overall probability of a sequence of events is derived from conditional probabilities which are characteristic of each single event and the outcome of a finite number of preceding events. (An obvious example of such a calculation would be the use of such derived, general relationships in the prediction of chemical composition of a copolymeric chain from the conditional probabilities which characterize the chemical combination of the various types of monomers and growing chain ends.) In contrast, the Monte Carlo method is essentially the simulation of a process or system by means of statistical "experiments" performed by applying appropriate mathematical operations to set of random numbers. (The Monte Carlo approach to the copolymer composition problem would be the direct use of the conditional probabilities to define intervals over the range of the random number, each interval corresponding to a possible outcome, *viz.*, choice of monomer to be added to a growing chain. The chain of representative composition is then generated merely by letting each choice be determined by the interval to which each random number is assigned on the basis of its magnitude.)

The first chapter, by G. G. Lowry, is a short introduction which includes definitions, general concepts, and a brief survey of current applications. These are worthwhile features, but the "reference" section on vectors and matrices is almost totally useless. If, for example, the reader is not already familiar with matrix eigenvalues and eigenvectors, the three sentences on this topic will be of little, if any, use. It would have been more realistic to refer such a reader to any of a number of books on matrix theory.

Chapter 2, by J. M. Myhre, is a very good introduction to the theory of Markov chains. The ideas are well presented and abstract concepts are illustrated by a large number of detailed examples involving simple systems. The following chapter, by M. Fluendy, serves the same purpose with regard to Monte Carlo theory. It is also well written, but perhaps contains too much detail with respect to the various tests for randomness in number sequences.

The first detailed discussion of an application of Markov chain theory, given in Chapter 4 by J. B. Kinsinger, is to the problem of chain conformation (spatial configuration). The ideas are clearly presented and a number of interesting results are given. It should be noted, however, that there is some disagreement on the extent to which Markoffian concepts are relevant to an actual *physical* chain; in this case, the "events" are states of a skeletal bond and the probabilities of such states must depend on succeeding as well as preceding states along the chain (P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969). Since vinyl polymer chains are treated in detail, it is disappointing that only the case of perfect stereoregularity is considered; treatment of vinyl chains of irregular structure would have provided an example of the use of both Monte Carlo calculations and Markov chain models to treat different aspects of the same problem.

An example of the utility of Monte Carlo calculations is given by S. Windwer in Chapter 5: the excluded volume problem in chain molecules is treated in some detail and a good summary of results to date is presented. Chapter 6, by J. Mazur, is an excellent, rather sophisticated treatment of Markov chains in which correlations extend over long sequences of events. Included in this chapter are good discussions of a variety of applications, and the relationship between Markov chains and Ising lattice models.

The composition of copolymers is treated by Markoffian statistics by F. P. Price in Chapter 7. His frequent comparison of the present treatment with the earlier (and more limited) kinetic approach will be very useful to many readers. The related problem of molecular weight distributions in polymers is treated by G. G. Lowry in the final chapter; the emphasis is on a Markoffian chain model, but the results of a number of Monte Carlo calculations are also given. The recent development of a number of experimental techniques for rapidly determining molecular weight distributions makes this final topic a very timely one.

It is a pleasure to recommend this book to anyone desiring information on the application of these important theoretical methods in polymer science.

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