merase and its presence on the surface of polyribosomes in HeLa cells, as shown by Smulson, indicated high activity of the enzyme on ribosomes during S phase of the cell cycle. Earlier L. Burzio and S. Koide [*Biochem. Biophys. Res. Commun.* **16,** 113 (1973)] showed that generation of the polymer in vitro in intact rat liver nuclei causes significant inhibition of the template capacity of the resultant DNA nuclear protein matrix of chromatin for DNA polymerase. This work has been extended in collaboration with K. Toshihara (Mara Medical University) by the observations that rat liver nuclei contain a Ca^{2+},Mg^{2+}-dependent endonuclease capable of "activating" rat liver CNA in vitro. Furthermore, it was shown that in the presence of semipurified poly(ADP-ribose) polymerase, DNA, and NAD, a short-chain modification is transferred to the endonuclease inactivating the enzyme and its ability to generate primer sites on DNA. This modification explains the apparent inhibition of DNA template activity in rat liver. An exonuclease from rat liver, which is inhibited by free chains of poly(ADP-ribose), has also been described by M. Yamada (Tokyo) and Sugimura.

In HeLa cells, however, Smulson showed that ADP-ribosylation of nuclear proteins leads to an enhancement rather than to an inhibition in the number of primer sites for DNA polymerase. This stimulation is inversely related to the natural extent of template restriction imposed by nuclear proteins during the cell cycle and cell proliferation. For example, chromatin seems very restricted for exogenous DNA polymerase early in the G1 phase, and ADP-ribosylation of nuclear proteins releases this restriction, at least in vitro.

Two other analogous ADP-ribosylation reactions occur naturally. Diphtheria toxin catalyzes a transfer of a single ADP-ribose unit from NAD to elongation factor 2, leading to inhibition of eukaryote protein synthesis. C. Edson, K. Ueda, and O. Hayaishi (Kyoto) and E. Maxwell, E. Robinson, and O. Henriksen (NIH) have been interested in the exact residue modified in EF-2. Maxwell's group has shown that ADP-ribose is linked to an unknown, weakly basic amino moiety which does not correspond to any known amino acid and which is part of unmodified EF-2 also.

Bacteriophage T4 infection of *Escherichia coli* leads to ADP-ribosylation of the α subunits of host RNA polymerase, presumably resulting in subtle changes in enzyme specificity. W. Zillig (West Germany) and C. Goff (England) both described their studies on the identification of ADP-ribosylated residues of the α subunit as well as in vitro assays for ultimate purification of the enzyme that effects this modification.

There is still much to be learned about the relation of these nonoxidative roles of NAD in cellular proliferation and regulation. Abstracts of this meeting on this topic will be published in the *Journal of Biochemistry (Tokyo)*.

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Organotransition-Metal Chemistry

Initial progress in the field of organotransition-metal chemistry has followed the lines of interest that were generated separately by organic and inorganic chemistry. However, it is increasingly clear that organotransition-metal chemistry is not only bridging these two fields but is also finding application in other branches of science.

The stabilization and isolation of both cyclobutadiene and benzene derivatives of transition-metal organometallics were first achieved because of academic interest. However, industrial processes, such as the Ziegler-Natta olefin polymerization, the Wacker oxidation of ethylene to aldehydes and ketones, and the hydroformylation of olefins, have provided practical applications for the achievements in organotransition-metal chemistry. Still to be determined is the exact role of transition-metal organometallics in many metal biological functions and processes—such as nitrogen fixation by nitrogenase and multifunctions of vitamin B_{12}—and the functions of organomercury as a pollutant, and catalytic functions in fuel cells.

During the past decade, Japanese organic chemists have focused on research on organometallic chemistry. As a result, Japanese organotransition-metal chemists have discovered new reactions and isolated unstable organotransition-metal compounds.

Detailed mechanisms for only a few reactions of organotransition metals are known. The seminar was devoted to the following specific themes: (i) factors influencing the stability of transition metal carbon bonds and mechanisms of the form and breaking of such bonds; (ii) features of the mechanisms of reactions involving unstable organotransition-metal complexes; (iii) application to catalytic processes, such as carbonylation and related processes in which both countries have some scientific and technological interest; and (iv) application to environmental problems, notably the formation of toxic organometallic compounds, such as methylmercury.

On 1 to 3 May 1974 the first Japanese-American seminar on Prospects in Organotransition-Metal Chemistry was held at the University of Hawaii's East-West Center, in Honolulu, jointly sponsored by the National Science Foundation and the Japan Society for the Promotion of Science. The purpose of the seminar was to acquaint participants with the major trends and directions of research in Japan and the United States. Attendance was limited to 17 Japanese and 24 Americans in order to encourage informal discussion and exchange of ideas between the two nationalities.

The first session, which dealt with novel organometallic compounds, was opened by the Japanese and American organizers of the conference, M. Tsutsui and Y. Ishii. Two participants from the University of California, Los Angeles, dealt with compounds of unusual geometry: M. F. Hawthorne discussed his work in polyhedral expansion and contraction of metallocarboranes, and H. D. Kaesz described unsaturated ruthenium hydridocarbonyl cluster complexes and their possible application to catalysis. Presentations of work on compounds with novel ligands were represented by K. Itoh (Nagoya University) on the bridging, bidentate behavior of benzoyl isocyanates and by R. B. King (University of Georgia) concerning complexes of polycyano-olefins, specifically comparing the dicyanovinylidene ligand with carbon monoxide. The actinide metals paper was presented by T. Marks (Northwestern University) on tris(cyclopentadienyl)alkyl complexes.

The largest single topic of interest was homogeneous catalysis. Although the original controversy over the concerted as compared to the stepwise mechanism of various metal-catalyzed rearrangements has been largely resolved, four papers on this subject were presented. First and foremost was R. Pettit's (University of Texas, Austin) very thorough presentation on the concerted nature of the rearrangement of polycyclic hydrocarbons catalyzed by silver ions. F. Mango (Shell Oil) and R. Grubbs (Michigan State University) each discussed metallocycles as intermediates in these reactions; Mango questioned whether any reaction proceeding in this way should really be called "concerted."

R. Noyori (Nagoya University) discussed his work on nickel(0)–catalyzed rearrangements involving highly strained σ bonds.

J. Halpern (University of Chicago), also active in research on homogeneous catalysis and a participant in the preceding discussion, presented a paper on a different aspect of catalysis—an analysis of the mechanism of catalysis by tris(triphenylphosphine)rhodium chloride. More specific applications of homogeneous catalysis were discussed by J. Kiji (Kyoto University) on diolefin polymerization catalyzed by Ni(0) complexes and acid, G. W. Parshall (DuPont) on activation (for exchange with deuterium gas) of aromatic C–H bonds, and J. Tsuji (Tokyo Institute of Technology) on addition reactions of butadiene catalyzed by palladium(II) complexes.

Two homogeneous catalytic reactions applicable to laboratory synthesis were presented: (i) M. Kumada (Kyoto University) discussed the efficient catalytic coupling of Grignard reagents with aromatic halides by phosphine complexes of nickel and (ii) Iwao Ojima (Sagami Chemicals) discussed the selective reduction of unsaturated ketones by rhodium-catalyzed hydrosilylation. The latter synthesis was also reported to have yielded products of up to 50 percent optical purity from racemic substrate and chiral catalyst.

One most unusual and timely report was that of J. Ibers (Northwestern University), who had observed that cationic rhodium phosphine complexes homogeneously catalyze the conversion of CO and NO to CO_2 and nitrogen.

In addition to the studies of catalytic reactions mentioned above, the kinetics and mechanism of several other reactions were presented. J. Osborn (Harvard) discussed the analysis of the oxidative addition of alkyl halides to Pt(0) and concluded that such reactions generally occur via radical chain pathways. A. Nakamura (Osaka University) examined the mechanism of a molybdenum dihydride complex with various unsaturated compounds, and T. Tanaka discussed his studies on the kinetics of TCNE addition to a cationic rhodium complex. G. Whitesides (Massachusetts Institute of Technology) covered two topics: (i) the decomposition mechanisms of metal alkyls and (ii) some results on synthetically useful Li-Hg-C complexes of unknown structure. Further discussions of metal alkyl complexes were heard. One concerned nuclear magnetic resonance studies of nickel-alkyl phosphine complexes by A. Yamamoto (Tokyo Institute of Technology), and a second the decarboxylation of allyloxycarbonyl platinum(II) complexes by H. Kurosawa (Osaka University).

Two investigators reported specifically on stereochemistry. K. Saito (Tohoku University) concentrated on the asymmetric induction arising upon coordination of an olefin to chloro-L-prolinato platinum(II), while J. Faller (Yale) lectured on the substituents required to prevent palladium-allyl chiral centers from racemizing.

The last session was devoted to biological aspects of organometallic chemistry, dealing chiefly with the metalloporphyrin and metallocorrin systems. J. Collman (Stanford) discussed a synthetic iron(II) porphyrin with a hydrophobic "pocket" in which oxygen could be reversibly absorbed. M. Tsutsui (Texas A & M) presented his work on some novel bimetallic rhenium porphyrins; H. Ogoshi (Kyoto University) also talked about noble metal porphyrins, considering their similarity to vitamin B_{12}. For the final paper, J. Wood (University of Illinois) presented his work on the mechanism of mercury neurotoxicity, which arises from methylmercury ion–catalyzed cleavage of a vinyl ether linkage found only in brain lipids.

The organizers are looking forward to another similar seminar 3 years hence, although a meeting location has not been selected. In comparing the Japanese and American contributions, the only general observation that might be made is that while the Japanese tended to collect more data, the Americans collected less, but analyzed it more thoroughly.

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Polyunsaturated Fatty Acids

The subject of the 1974 Deuel Lipid Conference, which took place at the Highlands Inn, Carmel, California, from 26 February to 2 March 1974, was a consideration of the polyunsaturated fatty acids from biochemical and medical points of view. The first session concerned the control mechanisms in the formation and transformations of the polyunsaturated fatty acids. R. Brenner from the University of La Plata, Argentina, discussed the location, nature, and control of the enzymes involved in fatty acid desaturation. Although all aerobic desaturation occurs in the endoplasmic reticulum and the cofactors are the same, there is good evidence that separate enzymes are responsible for desaturation at the Δ^4, Δ^5, Δ^6, and Δ^9 positions of the fatty acids and that there may be some chain-length specificity as well. Of the various desaturases, the Δ^6 enzyme may be the most important because, since it operates at the slowest rate, it serves as a control point of subsequent elongation and desaturation. Thus, in the important series of reactions leading from linoleic to arachidonic acid, the desaturation of linoleic acid to 6,9,12-octadecatrienoic acid appears to be the control point. The desaturation reaction requires cytochrome b_5 reductase, cytochrome b_5, and a cyanide-sensitive factor, which are intimately bound to the lipid bilayer of the endoplasmic reticulum. Furthermore, it requires a factor loosely bound to this membrane. This factor appears to be a protein, but its structure and function are not yet apparent.

Elongation and desaturation in higher plants was discussed by P. Stumpf of the University of California at Davis. He has found that, although the desaturation pathway leading from stearate through oleate to linoleate follows the usual aerobic desaturation mechanism of the ACP derivatives, the formation of the linolenic acid (a trienoic acid) occurs by desaturation at the C_{12} stage followed by elongation to C_{18} with a series of specific enzymes.

A. Fulco of the University of California, Los Angeles, reviewed his findings on the temperature-dependent regulation of Δ^5 unsaturated fatty acid biosynthesis in bacilli. In *Bacillus megaterium* an increasing rate of inactivation of the Δ^5 desaturase with increasing temperature appears to be the most important factor in determining the degree of Δ^5 desaturation during culture growth at a given constant temperature. In contrast, a sudden downward shift in growth or incubation temperature (for example, from 35° to 20°C) triggers a transitory hyperinduction of the Δ^5 desaturase, a process which is eventually shut off by a repressor and whose synthesis and stability is also governed by temperature. The greater the magnitude of the downward temperature shift, the longer the period of hyperinduction before repression becomes effective. Desaturase hyperinduction can be blocked by protein-synthesis inhibitors added before, or at the time of the temperature shift while repression (but no hyperinduction) is prevented by inhibitors of DNA synthesis added before the shift from 35° to 20°C.

The second session concerned the physiological effects of the essential fatty acids (EFA). R. B. Alfin-Slater of UCLA re-