PROFESSOR OTSUKA'S WORK AND ITS MEANING FOR THE SCIENTIFIC COMMUNITY

The early sixties was the period when the chemical industry started to produce polyolefins and polydienes by the Ziegler—Natta process, which enticed many chemists to become involved in this new field of organometallic chemistry and homogeneous catalysis. Having obtained a Professorship at Osaka University in the middle sixties, Professor Otsuka commenced synthetic exploratory studies in the, then infant, field of organometallic chemistry. The key ligand he chose was a somewhat bulky, biphilic compound, t-BuNC, which was prepared by his new method from hydrogen cyanide and isobutene. Owing to its ability to stabilize a wide range of transition metals in a variety of oxidation states and because of its spectroscopic tractability, he and his coworkers were able to synthesize and characterize a number of complexes of nickel, cobalt, palladium and other metals. Their success undoubtedly created many followers; the use of this particular isocyanide ligand has since become popular.

He was also interested in allene and oligoallene complexes, which were practically unknown then. At a later stage (the late seventies), he and his collaborators were able to prepare a series of 14 electron compounds, i.e. PdL_2, PtL_2 and RhHL, where L is a bulky electron-donating phosphine like $P(t\text{-}Bu)_3$, $P(Cyclohexyl)_3$, or $P(i\text{-}Pr)_3$. The existence of the two-coordinate species, which was established by X-ray analysis, surprised many chemists who believed that only 16 and 18 electron complexes should be obtainable.

What was the impetus? He says: "There are many aesthetically beautiful molecules in metal complexes. If they are inert, however, they do not attract me very much. According to my definition, inert complexes are in a way dead. I want to have lively molecules and to let them work." This philosophy is reflected in many of his papers. For example, isolating several unstable oligoallenenickel complexes, he was able to show how a Ni—L fragment acts as a template for selective oligomerization of allene leading to its cyclic trimer, tetramer or pentamer. The dioxygen nickel complexes NiO_2L_2 (L = t-BuNC, PR_3) are also unstable and reactive. His group was the first to investigate systematically the reactivity of η^2-O_2 on a metal, and to observe the nickel-catalysed oxygenation of t-BuNC to t-BuNCO.

The discovery of the low-coordinate complexes of platinum(0) and rhodium(0) was followed by a series of most exciting papers on the activation of water molecules. Unprecedented was the observation of oxidative addition of water to PtL_2 or $RhHL_2$ to yield hydridohydroxo complexes; strong bases resulted from two-electron transfer from the metal to H_2O. After completion of a quantitative study on the oxidative addition, his group developed several catalytic reactions based on this system. An efficient water-gas-shift catalysis was observed with $RhHL_2/H_2O$ systems. The reverse water-gas-shift reaction was also found; the reduction of CO_2 with $RhHL_2/H_2O$ to a CO ligand was amazingly facile, albeit stoichiometric.

One of his latest interests appears to be focused on asymmetric syntheses. A chiral cobalt-catalysed carbenoid reaction leading to optically active cyclopropane derivatives was found to proceed in a high optical yield (max. 88% ee), and a very extensive mechanistic study detailing the chirality of the induction was published. The most beautiful catalytic reaction of allylamine isomerizations to the corresponding enamine, an aldehyde synthon, was recently found by his group. The virtually perfect enantionface selectivity and the very high catalytic turn-over number of his rhodium catalyst, $[Rh((R)\text{- or }(S)\text{-binap})(diene)]^+$, are especially impressive. This catalytic reaction enables one to obtain citronellal with an optical purity exceeding that of the natural one. This discovery would certainly give an impact not only to academic research on homogeneous catalysis but also to industry. Commercial production of *l*-menthol based on this catalytic reaction started in 1983 in Japan. The process should also be a breakthrough for economical preparation of vitamin E.

His interest spreads over an unusually broad range. A number of new types of thiolatomolybdenum complexes, including dinuclear molecules and clusters, were prepared from the labile starting material $Mo(t\text{-}BuS)_4$, which was first made by his group. They have also worked on native dioxygenases and their model reactions. His achievements are so diverse that it is impossible to detail them all here. We truly hope he will continue his research after his formal retirement at the age of 63, which took place in 1982.

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I would like to list the following papers representing the most characteristic works of Prof. S. Otsuka.

1 Chemistry of Metal Complexes of Small Molecules such as Dihydrogen, Dioxygen, Isocyanides, etc., J. Am. Chem. Soc., 91 (1969) 6994; 95 (1973) 7262.
2 Asymmetric Catalysis, J. Am. Chem. Soc., 100 (1978) 3443.
3 Catalysis of Organometallic Complexes for Polymerization and Oligomerization of Dienes, Adv. Organomet. Chem., 14 (1976) 245.
4 Chemistry of Metal Complexes of Bulky Phosphines. J. Organomet. Chem., 200 (1980) 191.