

Diethylbis(dipyridyl)cobalt. A butadiene dimerization catalyst

Dimerization of butadiene to 3-methylhepta-1,4,6-triene by use of mixed catalyst systems containing cobalt compounds and triethylaluminum has been reported¹⁻³. In these catalyst systems, the formation of an ethylcobalt complex was postulated as the reaction intermediate⁴ but no such compounds have been isolated owing to the instability of carbon-cobalt σ -bonds. Synthesis of alkylcobalt complexes with several stabilizing ligands have been reported by Schrauzer and Kohnle⁵, Dolphin and Johnson⁶, Yamazaki and Hagihara⁷, and King⁸. We have found that α, α' -dipyridyl is an excellent stabilizing ligand for organotransition metal complexes and have succeeded in the isolation of σ -ethyl dipyridyl complexes of iron and nickel which catalyze the cyclooligomerization of butadiene⁹.

We wish to report now the preparation of a similar crystalline ethylcobalt complex which has the same catalytic activity for linear dimerization of butadiene as the mixed catalyst system².

The complex was obtained by the reaction of cobalt(III) acetylacetonate, α, α' -dipyridyl, and diethylaluminum monoethoxide in ether at $-10 \sim 10^\circ$. The needles separated out of the reaction mixture were washed repeatedly with absolute ether or hexane under rigorous exclusion of oxygen. The yield of the complex based on $\text{Co}(\text{acac})_3$ was *ca.* 85%. The complex is very air-sensitive and slightly soluble in benzene, ether and some other organic solvents. The electronic absorption spectrum of the benzene solution has absorption maxima at 585 $m\mu$ (ϵ 3900) and at 900 $m\mu$ (ϵ 1100). The results of elemental analysis, pyrolysis, and the reactions with water, alcohol and iodine were in agreement with the formula, $\text{Et}_2\text{Co}(\text{dipy})_2$. (Found: C, 66.16; H, 6.32; Co, 14.4. $\text{C}_{24}\text{H}_{28}\text{N}_4\text{Co}$ calcd.: C, 67.15; H, 6.05; Co, 13.74%.)

The reaction of the complex with iodine in benzene gave a reddish-brown compound, the iodine content of which was 39.81% (calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{CoI}_2$, 40.60%).

The complex begins to decompose around 50° . Ethane and ethylene in a ratio of *ca.* 2:1, trace amounts of hydrocarbons higher than C_4 and a residue were obtained by heating up to 160° . The volume of the gaseous products amounted to 1.4 moles/mole of the complex. The reactions with water and alcohol gave only ethane. We tentatively propose the structure of the complex to be as shown in Fig. 1. The *cis* structure is the alternative.

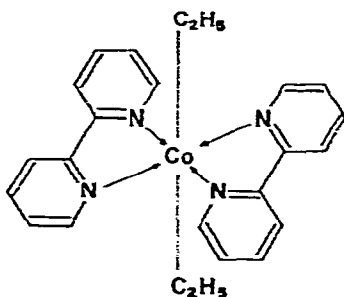
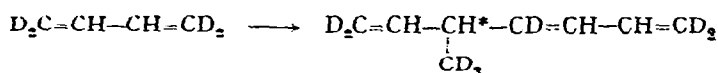


Fig. 1. Structure of $\text{Et}_2\text{Co}(\text{dipy})_2$ (*trans* form).

Dimerization of butadiene with a catalytic amount of the isolated complex was carried out in benzene at 50° and 3-methylhepta-1,4,6-triene was obtained as the main

product. The product of butadiene-1,1,4,4- d_4 dimerization was confirmed by its NMR spectrum together with other evidence to be 3-methyl- d_3 -hepta-1,4,6-triene-1,1,4,7,7- d_5 . The NMR spectrum of the deuterio-methylheptatriene as compared with that of 3-methylhepta-1,4,6-triene indicated the absence of the doublet (τ 8.90) assigned to the methyl protons, the change of the sextet (τ 7.15) into the doublet assigned to H* and the simplification of the multiplets of vinyl protons. The result suggests that the hydrogen transfer in the linear dimerization of butadiene by the cobalt complex catalyst occurs only at 1- and 4-positions of butadiene.



Department of Industrial Chemistry,
University of Tokyo,
Hongo, Tokyo (Japan)
Tokyo Institute of Technology,
Research Laboratory of Resources
Utilization, Meguro, Tokyo (Japan)

TARO SAITO
YASUZO UCHIDA
AKIRA MISONO
AKIO YAMAMOTO
KAZUHIKO MORIFUJI
SAKUJI IKEDA

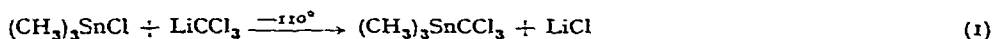
- 1 S. OHTSUKA, T. TAKETOMI AND T. KIKUCHI, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 66 (1963) 1094.
- 2 T. SAITO, T. OHNO, Y. UCHIDA AND A. MISONO, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 66 (1963) 1099.
- 3 S. TANAKA, K. MABUCHI AND N. SHIMAZAKI, *J. Org. Chem.*, 29 (1964) 1626.
- 4 S. OHTSUKA, T. KIKUCHI, Y. TANAKA, F. IMAIZUMI AND K. MORI, *The Chemistry of High Polymers (Japan)*, 22 (1965) 24.
- 5 G. N. SCHRAUZER AND J. KOHNLE, *Chem. Ber.*, 97 (1964) 3056.
- 6 D. DOLPHIN AND A. W. JOHNSON, *Chem. Commun.*, (1965) 494.
- 7 H. YAMAZAKI AND N. HAGIHARA, *Bull. Chem. Soc. Japan*, 38 (1965) 2212.
- 8 R. B. KING, *Inorg. Chem.*, 5 (1966) 82.
- 9 A. YAMAMOTO, K. MORIFUJI, S. IKEDA, T. SAITO, Y. UCHIDA AND A. MISONO, *J. Am. Chem. Soc.*, 87 (1965) 4652.

Received June 27th, 1966

J. Organometal. Chem., 6 (1966) 572-573

Halogenated organotin compounds as CX₂ transfer agents

We have expended considerable effort on studies of the CX₂ transfer reactions of phenyl(trihalomethyl)mercury compounds¹, and it seemed of interest to evaluate trihalomethyl compounds of other metals as dihalocarbene sources. The earlier work of Clark and Willis² showed trimethyl(trifluoromethyl)tin to be a source of CF₂ at 140-150°. This suggested that other trihalomethyltin compounds should undergo thermal α -elimination of trimethyltin halide to give dihalocarbenes, and we chose to commence our investigation of this aspect of halomethyl metal chemistry with a study of trimethyl(trichloromethyl)tin and trimethyl(bromodichloromethyl)tin. The preparation of the former was accomplished in 62 % yield using the reaction of trimethyltin chloride with trichloromethyl lithium³⁻⁵ (eqn. 1). A route to (CH₃)₃SnCCl₂Br was provided



J. Organometal. Chem., 6 (1966) 573-576