Catalysis of Hydridobis[bis(diphenylphosphino)ethane]cobalt in the Reaction of Butadiene with Ethylene

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A CATALYST consisting of dichlorobis[bis(diphenylphosphino)ethane]cobalt, [$CoCl_2(DP)_2$], and triethylaluminium is very effective for selective synthesis of hexa-1,4-diene from butadiene and ethylene.[1] Hexa-1,4-diene is formed as a result of shifting a hydrogen atom from ethylene to butadiene. In one of the possible mechanisms for the hydrogen shift, we assumed that a cobalt hydride complex is formed as a reaction intermediate, because cobalt hydride is easily formed and often acts as a hydrogen carrier.

Here we report the catalytic behaviour of hydridobis[bis(diphenylphosphino)ethane]cobalt in the above reaction. $CoCl_2(DP)_2$ with diethylaluminium ethoxide or with lithium aluminium hydride[2] yields the hydrido-cobalt complex, yet is inactive in the formation of hexa-1,4-diene,[3] probably because the cobalt is co-ordinately saturated. However, we find that certain substances can activate the hydrido-cobalt complex.

The results of adding a variety of organoaluminium compounds as the activator are shown in the Table. In systems containing $CoCl_2(DP)_2$, triethylaluminium was one of the most suitable co-catalysts, but in systems containing the hydrido-cobalt complex diethylaluminium chloride was more effective than triethylaluminium. Diethylaluminium ethoxide is able to reduce $CoCl_2$-$(DP)_2$ to yield the hydrido-cobalt complex, but does not activate it. Triethylaluminium used with $CoCl_2(DP)_2$ is considered to act as reducing reagent and as a moderate activator. Diethylaluminium chloride being a slightly poorer reducing agent was less effective in combination with $CoCl_2$-$(DP)_2$, but showed a high ability for the activation

TABLE

Catalysis of hydridobis[bis(diphenylphosphino)ethane]cobalt in the reaction of butadiene with ethylene[a]

No.	Activator (g.)	Toluene (ml.)	Temp. (°)	Time (hr.)	Butadiene (g.)	Ethylene (kg./cm.^{2})	Products (g.) 1,4-HD[b]	Others[c]	Residue
1	—	30	80	7·5	20·1	50	0·01	0·07	0·1
2	Et_3Al (0·83)	20	85	3·0	73·7	35	51·2	3·3	3·6
3	Et_2AlCl (0·48)	20	95	0·5	40·2	50	59·3	1·5	1·3
4	$Et_3Al_2Cl_3$ (0·25)	20	95	1·0	40·2	50	57·8	3·4	2·6
5	$AlCl_3$ (1·0)	20	105	2·0	33·5	40	14·7	0·08	22·6
6	PhOH (4·7)	50	90	17·0	33·5	45	27·8	—	3·1
7	*p*-$Cl{\cdot}C_6H_4{\cdot}OH$ (6·4)	50	90	17·0	33·5	45	48·6	0·5	5·2
8	2,4-$Cl_2{\cdot}C_6H_3{\cdot}OH$ (7·65)	50	85	18·0	33·5	45	44·8	—	7·8
9	2,4,5-$Cl_3{\cdot}C_6H_2{\cdot}OH$ (9·87)	50	85	18·0	36·8	45	47·2	0·6	10·7

[a] The hydrido-cobalt complex, 0·42 g.; [b] HD = hexadiene; [c] Contained the 2,4-isomer and higher oligomers.

of the hydrido-cobalt complex. The effects of organoaluminium compounds appear to be connected with their acidities.[4] Some typical Lewis acids were also activators, but many polymeric substances were simultaneously formed by cationic polymerization of butadiene.

Interestingly phenols are effective co-catalysts with the hydrido-cobalt complex. *p*-Chloro-, 2,4-dichloro-, and 2,4,5-trichloro-phenol are more effective than phenol, but 2,4,6-trichlorophenol is inactive. Since the hydrido-cobalt complex dissolved in the phenols used above, this may partly account for the activation but it is not a sufficient condition because 2,4,6-trichlorophenol also dissolved the complex.

We suggest that acidic compounds such as diethylaluminium chloride and aluminium chloride attack the basic moiety, probably a phosphorous atom co-ordinated with the cobalt atom, thus producing co-ordinative unsaturation and a position for attachment of the olefin. The action of the phenolic compounds is rather complicated. Their effectiveness depends on their acidity and the substituent effects.

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[1] A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, The 7th World Petroleum Congress, P.D. No. 22 (3), Mexico, 1967.

[2] A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274.

[3] M. Iwamoto and S. Yuguchi, *Bull. Chem. Soc. Japan*, to be published.

[4] (a) H. Imai, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, 1965, **81**, 92; (b) H. Lehmkuhl, *Angew. Chem., Internat. Edn.*, 1964, **3**, 107.