FACILE PHOTOGENERATION OF COORDINATIVELY UNSATURATED ACTIVE SPECIES FROM A HYDRIDOPHOSPHONITECOBALT(I) COMPLEX AND ITS APPLICATION TO DOUBLE-BOND MIGRATION OF OLEFIN

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Pyrex-filtered irradiation of a thermally inert complex  $[CoH{PPh-(OMe)}_2]_4]$  dissociated PPh $(OMe)_2$  from cobalt without cleavage of a hydrido-cobalt bond, yielding an active species "CoH $[PPh(OMe)_2]_3$ ". The photogenerated species caused double-bond migration of 3-phenylpropene to (E)- and (Z)-1-phenylpropenes.

Hydridocobalt(I) complexes supported by tertiary phosphines were very active as catalysts in hydrogenation,<sup>1-3</sup> oligomerization,<sup>1,4</sup> double-bond migration,<sup>1</sup>) and *cis-trans* isomerization<sup>5</sup> of olefins. In case of phosphite complexes [CoH-{P(OR)<sub>3</sub>}<sub>4</sub>], coordinatively unsaturated species such as "CoH[P(OR)<sub>3</sub>]<sub>3</sub>" were not produced under usual mild conditions and low catalytic activity of the complexes was associated with poor lability of the phosphite ligands.<sup>6,7</sup> However, there were reports on catalytic hydrogenation performed with  $[Co(n^3-c_3H_5){P(OMe)_3}_3]^8$  and  $[CoH(NCMe){P(OPh)_3}_3],^9$  and their true catalytic species were suggested to be "CoH[P(OMe)<sub>3</sub>]<sub>2</sub>" and "CoH[P(OPh)<sub>3</sub>]<sub>3</sub>" respectively. In the marked contrast to the above-mentioned phosphine or phosphite complexes which are air-sensitive, no attempt has been described on generation of catalytic active species from very stable hydridophosphonitecobalt(I) complexes  $[CoH{PPh(OR)_2}_4]$  and on synthetic utilization of the species in catalytic reactions. This communication deals with photochemistry of the hydridophosphonitecobalt(I) complexes and application of photogenerated species to double-bond migration of olefins.

A complex  $[CoH{PPh(OMe)}_{2}_{4}]^{10,11}$  was mixed with approximately four-fold moles

of PPh(OEt)<sub>2</sub> in degassed benzene solutions, and irradiation of the mixture was performed for 4 h at ca. 30°C at a distance of 75 mm from a 400 W high-pressure Hg lamp equipped with a Pyrex filter. A yellowish residue was obtained after removal of benzene and uncomplexed phosphonites under vacuum. A <sup>1</sup>H-NMR spectrum of [CoH-{PPh(OMe)<sub>2</sub>}<sub>4</sub>] in benzene showed a hydrido signal at  $\delta$  -14.1 as a quintet {J(PH)= 22 Hz}, and the quintet splitting was consistent with fast exchange<sup>12</sup>) of four phosphonite ligands on cobalt and spectroscopic equivalence<sup>12</sup>) of four <sup>31</sup>P nuclei. After irradiation of the mixture of the complex and PPh(OEt)<sub>2</sub>, the yellowish residue gave a complex signal which looked like two overlapping quintets. New signalpattern probably suggested coexistence of two kinds of coordinated phosphonites and similar fast exchange of the phosphonites on cobalt.

A mass spectrum of the yellowish residue revealed that it was a mixture of five hydridocobalt(I) complexes  $[CoH{PPh(OMe)}_2]_n{PPh(OEt)}_2]_{4-n}]$  (n=4,3,2,1,0). Table 1 shows their relative abundances derived from peak-heights of parent-ions, and no peaks were observed in the region above these parent-ions. The relative abundances suggested scrambling of about 81% of added PPh(OEt)<sub>2</sub> with PPh(OMe)<sub>2</sub> on cobalt. On the other hand, after 4 h without irradiation a small amount of  $[CoH{PPh(OMe)}_2]_3^ \{PPh(OEt)_2\}$  was produced together with a trace of  $[CoH{PPh(OMe)}_2]_2\{PPh(OEt)_2]_2$ , and there were no signals attributable to complexes  $[CoH{PPh(OMe)}_2]_n\{PPh(OEt)_2]_4-n]$  (n=1,0). It was concluded that irradiation caused dissociation of a phosphonite ligand from cobalt efficiently without cleavage of the hydrido-cobalt bond, and produced a coordinatively unsaturated species "CoH[PPh(OMe)\_2]\_3"

	Relative Abundances (%), <sup>b)</sup> Observed (Corrected <sup>c)</sup> )						
	m/e	740	768	796	824	852	
		(n=4)	(n=3)	(n=2)	(n=1)	(n=0)	
Irradiation <sup>d)</sup>		11(9)	29(26)	39(40)	18(21)	3(4)	
Dark		84(82)	16(18)	trace	_	-	

Table 1. Mass Spectra of a Mixture of  $[CoH{PPh(OMe)_2}_n{PPh(OEt)_2}_{4-n}]^a$ 

a) Formed in degassed benzene solutions of  $[CoH{PPh(OMe)}_2]_4]$  (4.7 × 10<sup>-3</sup> mol dm<sup>-3</sup>) and PPh(OEt)<sub>2</sub> (1.9 × 10<sup>-2</sup> mol dm<sup>-3</sup>) at ca. 30°C after 4 h.

b) Mass spectra : Parent-ions of the complexes were measured at 100~120°C to determine the relative abundances.

c) Corrected by factors due to slightly different properties of ionization and volatility of the complexes. See ref. 13.

d) Irradiation was performed at a distance of 75 mm from the Hg lamp.

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hydridocobalt(I) complexes with two kinds of phosphonites.

In view of facile photogeneration of the coordinatively unsaturated hydride species from the thermally inert complex  $[CoH\{PPh(OMe)_2\}_4]$  and prospect of successful utilization of the species as a catalyst, we studied photoassisted double-bond migration of 3-phenylpropene to (E)- and (Z)-1-phenylpropenes.

A mixture of the hydridocobalt(I) complex and 3-phenylpropene was irradiated at a distance of ca. 45 mm from the Hg lamp, and the reaction was monitered by gas chromatography. 3-Phenylpropene alone was not isomerized to (E)- and (Z)-1phenylpropenes after 8 h under irradiation. Moreover, photoisomerization of 3phenylpropene did not occur in the presence of free phosphonite. In the dark, the hydridocobalt(I) complex did not convert 3-phenylpropene to 1-phenylpropenes at all at ca. 30°C. However, under irradiation the complex caused double-bond migration of 3-phenylpropene to (E)- and (Z)-1-phenylpropenes, as shown in Table 2. No other products such as propylbenzene were detected on the basis of gas chromatography. When irradiation of the mixture of the complex and 3-phenylpropene was stopped, the double-bond migration of 3-phenylpropene ceased immediately. Accordingly, the migration was virtually "photoassisted" rather than "true photocatalytic". 14)

In connection with the above-described photochemistry of the hydridocobalt(I)

Additive <sup>b)</sup> and Reaction Conditions			Product Distribution (%) <sup>d)</sup>				
			3-phenylpropene (remaining)	1-phenylpropene E Z			
$[CoH{PPh(OMe)_2}_4]$	dark	8 h	~100	trace			
$[CoH{PPh(OMe)_2}_4]$	irradiation <sup>C)</sup>	4 h	59.9	34.5	5.7		
$[CoH{PPh(OMe)_2}_4]$	irradiation <sup>c)</sup>	8 h	31.0	59.5	9.5		
None	irradiation <sup>C)</sup>	8 h	100	0	0		
PPh(OMe) <sub>2</sub>	irradiation <sup>C)</sup>	8 h	100	0	0		

								2)
Table 2.	. Double-bond	Migration	of	3-Phenylpropene	to	1-Phenylpropenes	at	30°C <sup>4</sup>

a) 3-Phenylpropene, 7.0  $\times$  10<sup>-2</sup> mol dm<sup>-3</sup>.

b)  $[CoH{PPh(OMe)_2}_4]$ ,  $1.4 \times 10^{-3}$  mol dm<sup>-3</sup>; PPh(OMe)<sub>2</sub>,  $1.4 \times 10^{-3}$  mol dm<sup>-3</sup>.

c) Degassed benzene solutions were irradiated at a distance of 45 mm from the Hg lamp.

d) Determined by GLC analysis.

complex, the observed photoassisted double-bond migration was explained reasonably by initial photogeneration of the species "CoH[PPh(OMe)<sub>2</sub>]<sub>3</sub>" allowing 3-phenylpropene to coordinate to cobalt, followed by positional isomerization of the olefin and dissociation of 1-phenylpropenes, which are thermodynamically more stable than 3phenylpropene. The positional isomerization of coordinated 3-phenylpropene was believed to involve insertion of the olefin into the hydrido-cobalt bond and  $\beta$ hydrogen elimination from an alkyl complex.

## References

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