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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,$^{1-3)}$ oligomerization,$^{1,4)}$ double-bond migration,$^{1)}$ and *cis-trans* isomerization$^{5)}$ of olefins. In case of phosphite complexes [CoH{P(OR)$_3$}$_4$], coordinatively unsaturated species such as "CoH[P(OR)$_3$]$_3$" were not produced under usual mild conditions and low catalytic activity of the complexes was associated with poor lability of the phosphite ligands.$^{6,7)}$ However, there were reports on catalytic hydrogenation performed with [Co(η^3-C$_3$H$_5$){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)$_3$]$_2$" and "CoH[P(OPh)$_3$]$_3$" 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 $PPh(OEt)_2$ 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 ^1H-NMR spectrum of $[CoH\{PPh(OMe)_2\}_4]$ in benzene showed a hydrido signal at δ -14.1 as a quintet {J(PH)= 22 Hz}, and the quintet splitting was consistent with fast exchange[12] of four phosphonite ligands on cobalt and spectroscopic equivalence[12] of four ^{31}P nuclei. After irradiation of the mixture of the complex and $PPh(OEt)_2$, the yellowish residue gave a complex signal which looked like two overlapping quintets. New signal-pattern 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 $PPh(OEt)_2$ with $PPh(OMe)_2$ 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 "$CoH[PPh(OMe)_2]_3$" to afford the

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

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

a) Formed in degassed benzene solutions of $[CoH\{PPh(OMe)_2\}_4]$ (4.7×10^{-3} mol dm^{-3}) and $PPh(OEt)_2$ (1.9×10^{-2} mol dm^{-3}) 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.

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)-1-phenylpropenes after 8 h under irradiation. Moreover, photoisomerization of 3-phenylpropene 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)

Table 2. Double-bond Migration of 3-Phenylpropene to 1-Phenylpropenes at 30°C[a)]

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

a) 3-Phenylpropene, 7.0×10^{-2} mol dm^{-3}.
b) $[CoH\{PPh(OMe)_2\}_4]$, 1.4×10^{-3} mol dm^{-3}; $PPh(OMe)_2$, 1.4×10^{-3} mol dm^{-3}.
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 "$\mathrm{CoH[PPh(OMe)_2]_3}$" 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 3-phenylpropene. The positional isomerization of coordinated 3-phenylpropene was believed to involve insertion of the olefin into the hydrido-cobalt bond and β-hydrogen elimination from an alkyl complex.

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