Chemical Reactivities of Coordinatively Unsaturated Hydridotris(phosphonite)cobalt(I) Species Photogenerated towards Allylic and Related Compounds

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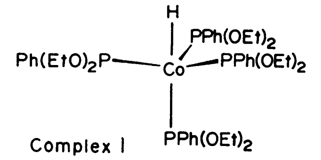
Pyrex-filtered photoirradiation with a high-pressure Hg lamp was performed for a thermally inert hydridocobalt(I) $CoH[PPh(OEt)_2]_4$ in the presence of some allylic compounds. Allyl benzoate and allyl phenyl ether showed the cleavage of allylic-O bonds to give propene in a stoichiometric quantity to the complex charged. Photoassisted catalytic double-bond migration occurred for *N*-allylacetamide, *N,N*-diethylallylamine, and allylbenzene to afford the respective (*E*)- and (*Z*)-1-propenyl derivatives with kinetically controlled *E, Z* compositions, and the fractions of *Z* isomers at the initial stage of the reaction proceeding were near 79, 30, and 20%, respectively. Laser flash photolysis study revealed that the double-bond migration was initiated by the coordination of the substrates through C=C double bond rather than nitrogen or oxygen donor-atom to the coordinatively unsaturated species "$CoH[PPh(OEt)_2]_3$" photogenerated.

Pyrex-filtered photoirradiation of a thermally inert hydridocobalt(I) complex $CoH[PPh(OR)_2]_4$ caused dissociation of a $PPh(OR)_2$ ligand from cobalt efficiently without cleavage of the hydrido-cobalt bond, and produced a coordinatively unsaturated hydrido species "$CoH[PPh(OR)_2]_3$."[1,2] Nitrogen-laser pulse excitation was also found to generate the hydrido species with a quantum yield of almost 1.0, and absolute rate constants were determined for coordination of free $PPh(OR)_2$ and some olefins to the species.[3] Furthermore, high catalytic activities of the hydrido species were realized in hydrogen transfer from secondary alcohols to ketones and isomerization of olefins.[1,4,5]

In the present paper, chemical reactivities of the hydrido species "$CoH[PPh(OEt)_2]_3$" ($CoHP_3$) photogenerated from $CoH[PPh(OEt)_2]_4$ (**1**) were studied towards some allylic compounds linked to heteroatoms or aromatic rings, which included *N*-allylacetamide, *N,N*-diethylallylamine, allylbenzene, allyl benzoate, and allyl phenyl ether. Incentive for studies on these reactions was derived from the following; (i) competitive coordination through two coexisting ligating sites i.e. the olefinic moiety and the heteroatoms with lone pairs of electrons to $CoHP_3$, (ii) chemical reactivities of $CoHP_3$ with the allylic compounds to cleave bonds between the allylic carbon and the heteroatoms,[6] and (iii) potential synthetic utility of catalytic olefin isomerization.[7] One of the authors (S.O.)[8] communicated that photoreaction of **1** with allyl phenyl ether gave almost equimolar quantity of propene to **1** charged and a small amount of 1-propenyl phenyl ether, and excluded initial coordination to $CoHP_3$ via the ether oxygen. As for nitrogen donor-ligands with higher coordination ability than ether oxygen, there were a few papers on formation of their cobalt(I) complexes.[9] It seems worthwhile to compare two ligating sites of the olefinic nitrogen compounds on coordination towards the transient $CoHP_3$ species, by means of laser flash photolysis.



Complex I

Experimental

Materials. *N,N*-Diethyl-1-propenylamine,[10] *N*-(1-propenyl)acetamide,[11] and *N*-allylacetamide[12] were prepared by the literature methods, and other allylic compounds and their isomerized 1-propenyl derivatives were commercially available. The complex $CoH[PPh(OEt)_2]_4$ **1** was prepared according to the Gray's method.[13] Benzene was treated with concentrated sulfuric acid until thiophenfree. After water washing, it was dried over anhydrous magnesium sulfate, and distilled from sodium under nitrogen. Toluene was purified similarly.

General Procedures. ^1H NMR spectra were recorded on a JEOL FX-90Q and a BRUKER AM-400 spectrometers. The gas chromatographic (GLC) analyses were performed on a SHIMADZU GC-8AIT (TCD) and a GC-8APF (FID) instruments. For irradiation, a high-pressure mercury lamp (400 W) was used with a Pyrex filter, and reactant solutions were placed at about 45 mm from the lamp.

Olefin Isomerization and GLC Analyses of the Products. Benzene solutions (5 cm^3) of **1** (0.04 mmol) and allylic compounds (0.8 mmol) were degassed by freeze-pump-thaw cycles in a Pyrex Schlenk tube (18 mm$^\phi$). After standing the solutions at 30 °C in the dark or under irradiation to proceed double-bond migration of the olefins, GLC analyses of gaseous products were performed using a Porapak Q or a molecular-sieve 5A column (3 m×3 mm$^\phi$) with a TCD detector, and other organic compounds were determined with a similar PEG-20M column and a FID detector.

Cis-trans isomerization of 1-propenyl derivatives was carried out analogously.

In the case of *N,N*-diethylallylamine, toluene was used as solvent for better resolution of GLC signals to evaluate conversion of the double-bond migration. However, determination of the *E, Z* composition in *N,N*-diethyl-1-propenylamine made it necessary to adopt ^1H NMR product analyses,

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as follows.

Reaction of *N,N*-Diethylallylamine or *N,N*-Diethyl-1-propenylamine and ^{1}H NMR Product Analyses. *N,N*-Diethylallylamine (0.8 mmol) was added to a C_6D_6 solution (0.6 cm^3) of **1** (0.04 mmol) and the mixture was degassed in a Schlenk tube (5 mm$^\phi$). After reaction at 10 °C, a small amount of tetramethylsilane was added to the mixture. Some quantity of the volatile components was separated from the nonvolatiles by trap-to-trap vacuum distillation without heating, and was sealed in NMR tubes under vacuum. The ^{1}H NMR spectrum of the distillate showed resonances for *E* and *Z* isomers of *N,N*-diethyl-1-propenylamine together with some unreacted *N,N*-diethylallylamine, and olefinic proton signals in the 1-propenylamines were useful for determination of the *E*/*Z* ratio.

Cis–trans isomerization of *N,N*-diethyl-1-propenylamine was performed similarly.

Laser Flash Photolysis. The apparatus of laser flash photolysis consists of a nitrogen laser (National Research Group, pulse width 5 ns, 4 mJ/pulse) for excitation at 337 nm, a 150 W xenon lamp (Ushio) for monitoring, a grating monochromator (Union Giken), a photomultiplier (Hamamatsu Photonics R446 or R212), a storage oscilloscope (Iwatsu TS-B123), and a personal computer (Sharp MZ-2000) for controlling the system, averaging the signal, and analyzing the data. A right-angle optical system was employed for the excitation-analysis set-up. An average of at least 9 shots, at each particular wavelength, was used for the determination of transient spectra or the investigation of reaction kinetics. The rate constants were determined according to the procedure of Ref. 16 and can be regarded as accurate to within ca. 10%. Solutions (5 cm^3) of **1** ($\approx$0.6 mM†††) and *N,N*-diethylpropylamine (1.0—6.4 M), *N,N*-diethylallylamine (13—47 mM), *N*-propylacetamide (0.108—0.51 M), or *N*-allylacetamide (1.9—11.7 mM) were purged of oxygen by bubbling with argon and subjected to laser flash photolysis at 23 °C. Toluene and benzene were used as solvents for the amines and the amides, respectively.

Results and Discussion

Photoassisted Double-Bond Migration of Olefins with the Hydridocobalt(I) Complex. The complex $CoH[PPh(OEt)_2]_4$ (**1**) was mixed with 20-fold moles of allylic compounds in deaerated benzene or toluene solutions. In the cases of *N*-allylacetamide, *N,N*-diethylallylamine, and allylbenzene, photoirradiation of the solutions led to their catalytic double-bond migration, yielding the corresponding (*E*)- and (*Z*)-1-propenyl derivatives, which are thermodynamically stabilized through π-conjugation with a lone electron pair on nitrogen or a delocalized π-system. Figure 1 shows plots of the conversions versus time for the double-bond migration of these compounds at 30 °C. The double-bond migration of *N*-allylacetamide proceeded well and was completed within 20 min. On the other hand, photoreactions of allyl benzoate and allyl phenyl ether for 6 h gave 1-propenyl derivatives with the conversions of only ca. 1 and 5%, respectively, and large quantities of unreacted substrates were recovered. However, propene was formed in the yields of 71 and 76% based on **1**, respectively. In the photocatalytic reaction with *N,N*-diethylallylamine, we detected only small amount of propene (1.6% based on **1**) together with traces of ethylene and ethane, whereas the reaction with *N*-allylacetamide did not yield propene at all.

$$RCH_2CH{=}CH_2 \xrightarrow{\text{Cat}} RCH{=}CH\text{-}CH_3$$

$$R = \text{-}NHCOCH_3,\quad \text{-}NEt_2,\quad \text{-}C_6H_5$$

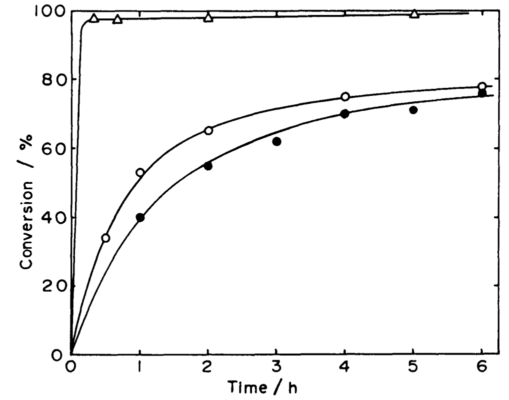

Fig. 1. Double-bond migration of allylic compounds to (*E*)- and (*Z*)-1-propenyl derivatives under irradiation with **1**.
At 30°C; Monitored by GLC; △: *N*-Allylacetamide, ○: *N,N*-Diethylallylamine, ●: Allylbenzene.

Allylic compounds did not afford propene or 1-propenyl derivatives under irradiation in the absence of **1**, and addition of free $PPh(OEt)_2$ did not change the situation either. Furthermore, neither double-bond migration nor propene formation occurred for the allylic compounds in the presence of **1** in the dark at 30 °C. These two types of reactions proceeded only in the presence of **1** under irradiation, and were attributed to operations of the photogenerated $CoHP_3$.

When irradiation of *N*-allylacetamide, *N,N*-diethylallylamine, and allylbenzene with **1** was stopped in the middle of the reaction proceeding, the double-bond migration ceased immediately. On restarting irradiation, the migration proceeded again. The double-bond migration of the present system was determined to be virtually "photoassisted" rather than "true photocatalytic."[14] The immediate cessation of the reaction proceeding upon interruption of irradiation was due to easy recombination of $CoHP_3$ with the photodissociated $PPh(OEt)_2$.[1,3] After incorporation of these allylic compounds with the photogenerated $CoHP_3$, insertion of their olefinic moieties into the hydridocobalt bond formed alkyl intermediates, which released (*E*)- and (*Z*)-1-propenyl derivatives through β-hydrogen abstraction by cobalt, and $CoHP_3$ was regenerated, as shown in Scheme.

Kurosawa[15] performed reactions of allylamines with some cationic platinum(II) hydrides, affording π-allyl

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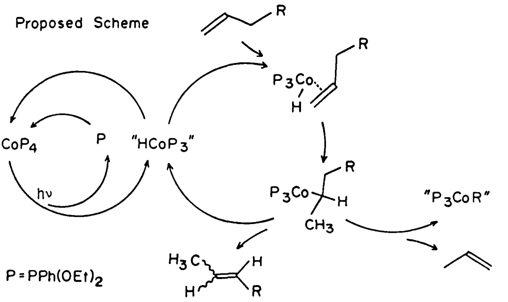
††† 1 M=1 mol dm^{-3}.

complexes and amine products through replacement of the allylic group in the parent amines with hydrogen, and suggested that allylamines ligated to platinum via the nitrogen atoms rather than via the C=C double-bond at the first stage. On the other hand, laser flash photolysis (vide infra) of the present system with **1** revealed the initial π-coordination of the C=C bonds to cobalt, leading to the catalytic double-bond migration under continuous irradiation. Furthermore, photoassisted double-bond migration of *N*-allylacetamide with **1** showed a sharp contrast to the case with the platinum(II) hydrides, which formed a catalytically inactive [1-(acetylamino)propyl-*C*^{1},*O*]platinum(II) complex.[15]

Photoirradiation of allyl benzoate and allyl phenyl ether in the presence of **1** would form alkyl intermediates similarly, but then alternative abstraction of β-benzoyloxy and β-phenoxy entities[8] by cobalt was presumed to occur as the major pathway, affording benzoato- and phenoxocobalt species with release of propene (Scheme). These cobalt species were not catalytically active, and the formation of propene was stoichiometric to **1** charged. Similar cleavage of allylic-O bonds in allylic carbonates and esters was observed by Yamamoto and his co-workers,[6h,6i] in reactions with some transition-metal hydrides without photoirradiation.



Coordination Process of Substrates to the CoHP$_3$ Species. Time-resolved absorption spectra were observed after laser flash photolysis of **1** in the presence of amides or amines, and second-order rate constants *k*′ were determined for coordination of substrates to the transient CoHP$_3$ species photoproduced. Photoisomerization of *N*-allylacetamide and *N*,*N*-diethylallylamine observed in the present study was presumed to involve their coordination of CoHP$_3$ as one of key processes in catalytic cycles, similarly to that communicated for allylbenzene.[1]

Amides and amines may coordinate to CoHP$_3$ through a lone electron pair of an oxygen or nitrogen donor-atom. In the case of a nonolefinic amide or amine, the transient absorption spectra showed both peak-decay of the band at 580 nm and peak-growth of the band in the region of about 450 to 420 nm, with formation of an isosbestic point (Figs. 2 and 3). The peak of the latter band grew almost on the same rate as the peak at 580 nm decayed (Table 1). On the other hand, in the case of an olefinic amide or amine, we observed only the peak-decay at 580 nm (Figs. 4 and 5). The band at 580 nm is attributed to the living CoHP$_3$ species, and its peak-decay was caused by the coordination of the substrates and by the recombination of CoHP$_3$ with the photodissociated PPh(OEt)$_2$.[3,8,16]

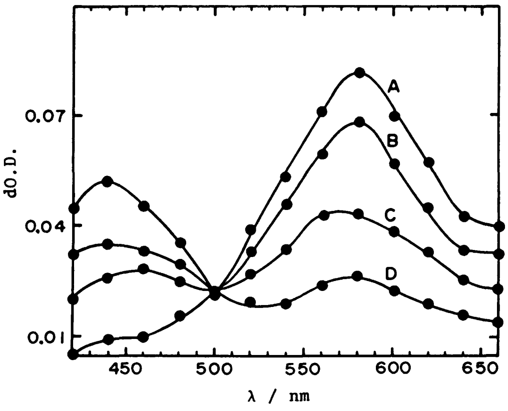


Fig. 2. Time-resolved absorption spectra for *N*-propylacetamide after pulsed laser photolysis. Substrate, 0.108 M (benzene); Complex **1**, 0.656 mM. A: 0.20 μs, B: 0.98 μs, C: 2.49 μs, D: 4.99 μs.

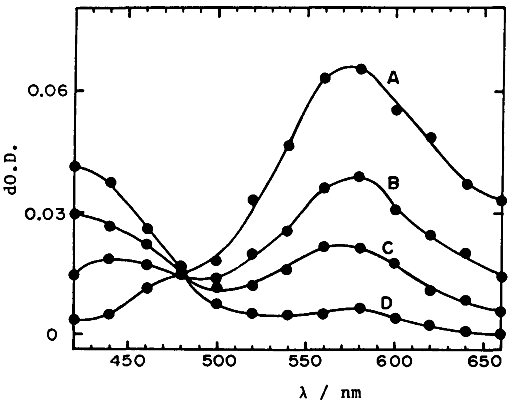
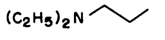
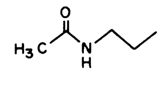
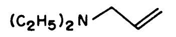
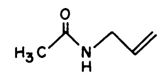


Fig. 3. Time-resolved absorption spectra for *N*,*N*-diethylpropylamine after pulsed laser photolysis. Substrate, 6.44 M (neat); Complex **1**, 0.656 mM. A: 0.82 μs, B: 4.49 μs, C: 8.79 μs, D: 20.0 μs.

Table 1. Second-Order Rate Constants *k*′ for Coordination ($M^{-1} s^{-1}$)[a]

	1.9×10^4 (1.9×10^4)		1.8×10^6 (2.1×10^6)
	4.7×10^7		1.9×10^8

a) Values were determined from the peak-decay at 580 nm, and those in the parentheses were obtained from the peak-growth in the region of about 450 to 420 nm; The rate constants *k*′ were evaluated from the following equation.[16]

$$-\frac{d[CoHP_3]}{dt}=k[CoHP_3][P]+k'[CoHP_3][Substrate]$$

The olefinic compounds, *N*-allylacetamide and *N,N*-diethylallylamine gave similar spectral change to that observed for 1-hexene or allylbenzene,[3,16] indicating the ligation to $CoHP_3$ via the double bond in a π-fashion, rather than via the oxygen or nitrogen donor-atom.

The peak-growth in the region of about 450 to 420 nm for the nonolefinic amide or amine was associated with formation of the new adducts of $CoHP_3$ with the substrates attached via the oxygen or nitrogen donor-atom. These donor-atoms have not empty low-lying orbitals appropriate for back donation bonding with metal, in contrast to $PPh(OEt)_2$ and the C=C double bond. Accordingly, absorption spectra of the hydridocobalt adducts with oxygen or nitrogen donor-ligands are expected to show red shifts of bands significantly from those of **1**.[17] On the other hand, absorption spectral change would be small on transformation from **1** to the adducts of $CoHP_3$ with olefins, and it is no wonder that we observed only the peak-decay of the band at 580 nm, attributable to $CoHP_3$, in the laser photolysis of **1** in the presence of the olefinic compounds.

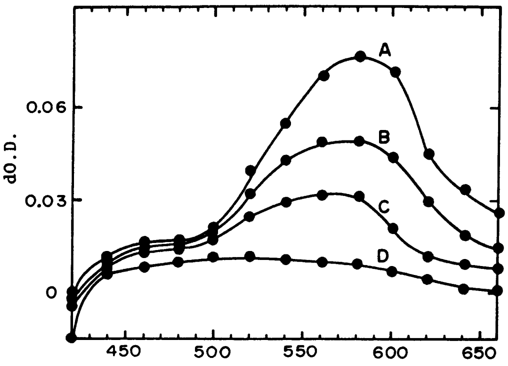


Fig. 4. Time-resolved absorption spectra for *N*-allylacetamide after pulsed laser photolysis. Substrate, 3.90 mM (benzene); Complex **1**, 0.656 mM. A: 0.29 μs, B: 0.98 μs, C: 1.76 μs, D: 4.39 μs.

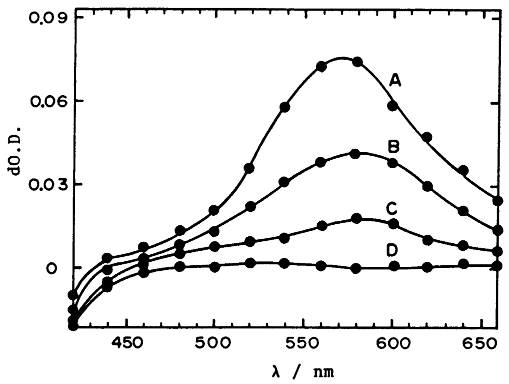


Fig. 5. Time-resolved absorption spectra for *N,N*-diethylallylamine after pulsed laser photolysis. Substrate, 20.1 mM (toluene); Complex **1**, 0.656 mM. A: 0.27 μs, B: 0.98 μs, C: 1.95 μs, D: 20.0 μs.

The rate constants *k′* of *N*-allylacetamide and *N,N*-diethylallylamine were comparable to those of 1-hexene and allylbenzene ($\approx 1.2 \times 10^8$ M^{-1} s^{-1}),[16] and were far larger than those of *N*-propylacetamide and *N,N*-diethylpropylamine, confirming the π-coordination of the allylic compounds via the C=C double bond.

***E,Z* Selectivity in 1-Propenyl Derivative Formation from Allylic Compounds.** 1-Propenyl compounds with several *E*/*Z* isomeric ratios were added in 20-fold molar quantities to deaerated solutions of the complex **1**, and their cis-trans isomerization was attempted. Table 2 summarizes the results of *N*-(1-propenyl)-acetamide, *N,N*-diethyl-1-propenylamine, and 1-propenylbenzene. Photoirradiation with **1** promoted the isomerization, and the fraction of *Z* isomer in each of the 1-propenyl compounds approached one equilibrium value at the photostationary state after prolonged irradiation. The *Z* fractions were 51±2, 2±2, and 2±1% for *N*-(1-propenyl)acetamide, *N,N*-diethyl-1-propenylamine, and 1-propenylbenzene, respectively. In several runs performed with the constant quantity of **1**, change of the amount of 1-propenyl compounds charged did not show any significant effect on the *Z* fractions at the photoassisted equilibrium.

Table 2. Cis-trans Isomerization of 1-Propenyl Derivatives[a)]

R	Analysis	Reaction Time	Reaction Temp	Z Fraction/% Before Reaction	Z Fraction/% After Reaction
		h	°C		
$-NHCOCH_3$	GLC	6	30	72±2	51±2
		6	30	22±1	52±2
$-N(C_2H_5)_2$	^{1}H NMR	5	10	27±2	12±2
		24	10	26±2	2±2
		24	10	2±2	2±2
$-C_6H_5$	GLC	5	30	61±2	23±1
		5	30	15±1	2±1
		14	30	35±2	2±1
		5	30	2±1	3±1

a) The cobalt(I) complex **1** (0.04 mmol) was mixed with the 1-propenyl derivatives (0.8 mmol) in benzene, and the mixture was irradiated. See the experimental section.

Table 3. *Z* Fraction of 1-Propenyl Derivatives Formed during the Early Stage from Allylic Compounds[a)]

R	Analysis	Temp	*Z* Fraction/% (Conversion/%)	
		°C	Experimental Values	Extrapolated Value[b)]
$-NHCOCH_3$	GLC	30	75±2 (5.4), 68±2 (14)	~79 (0)
$-N(C_2H_5)_2$	^1H NMR	10	26±2 (20), 24±2 (30)	~30 (0)
$-C_6H_5$	GLC	30	20±4 (1.3), 26±2 (17), 24±2 (27)	~20 (0)

a) The cobalt(I) complex **1** (0.04 mmol) was mixed with the allylic compounds (0.8 mmol) in benzene, and the mixture was irradiated. See the experimental section. b) These values were obtained by extrapolating plots of the experimental value vs. conversion to the intercept at zero conversion.

In consideration of absorption spectra of **1** and the 1-propenyl compounds and of the radiation spectrum from the Hg lamp equipped with the Pyrex filter, the line at 366 nm and its trailing part were mainly responsible for the photoreactions with **1**, and incident photons in this wavelength region were absorbed almost completely by **1**. Thus, direct cis-trans photoisomerization of the 1-propenyl compounds without intervention of the $CoHP_3$ species, was presumed to make relatively small contribution to the photoassisted equilibrium states. Main contribution to the states was believed to be thermodynamically equilibrated interconversion between two isomers of the respective 1-propenyl compounds. For *N*-(1-propenyl)-acetamide and 1-propenylbenzene, the cis-trans isomerization was not observed in the presence of **1** in the dark at 30 °C, and hence the thermodynamic interconversion was assumed to occur actually only under assistance of $CoHP_3$ photogenerated. On the other hand, the *Z* isomer of *N,N*-diethyl-1-propenylamine is thermally labile, and prolonged standing at 10 °C converted it slowly to *E* isomer. Photoirradiation of the *Z* isomer in the presence of **1** enhanced the isomerization rate considerably.

As for the double-bond migration of allylic compounds, Table 3 shows the *Z* fractions in 1-propenyl derivatives formed during the early stage of the reaction proceeding. The *Z* fractions extrapolated back near zero conversions were approximately 79, 30, and 20% for the reactions of *N*-allylacetamide, *N,N*-diethylallylamine, and allylbenzene, respectively. These numerical values were considerably different from those of the above-described photoassisted equilibrium for the cis-trans isomerization of the 1-propenyl compounds. Accordingly, the present double-bond migration was determined to yield kinetically controlled products of the 1-propenyl derivatives.

In the course of the double-bond migration, allylic compounds were allowed to coordinate to $CoHP_3$ photoproduced, and insertion of the olefins into the hydrido-cobalt bond probably followed to form alkyl intermediates (Scheme). At the stage immediately before conversion of the intermediates to $CoHP_3$ and product olefins through *β*-hydrogen elimination, steric interactions within the alkylmetal groups would favor an eclipsed transient conformation A (Fig. 6), which is expected to yield *E* isomer of product olefins predominantly. This was probably the case for *N,N*-diethylallylamine and allylbenzene. However, in case of *N*-allylacetamide, we believed that probable additional weak interaction[18)] of the amide oxygen with cobalt in the alkyl intermediate enhanced steric interactions between the alkyl group and other coexisting ligands on cobalt significantly, causing preferential formation of the transient conformation B to release the *Z* isomer mainly.

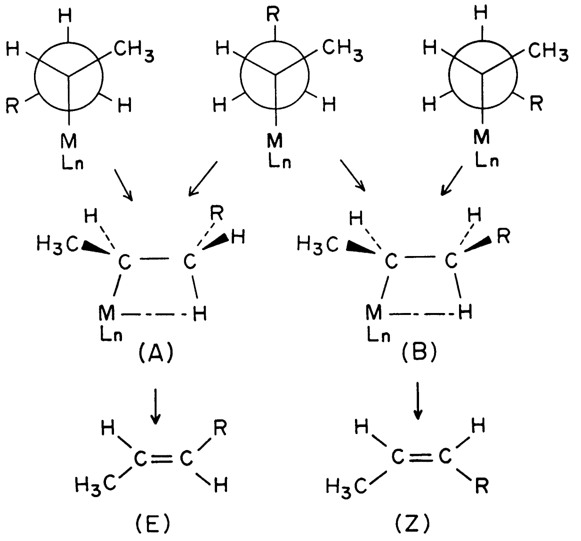


Fig. 6. *β*-Hydrogen elimination from the alkyl intermediates.

Concluding Remarks

The $CoHP_3$ species, photogenerated from the thermally inert hydridocobalt(I) **1**, cleaved the allylic-O bonds in allyl benzoate and allyl phenyl ether with release of propene, whereas the species catalyzed the double-bond migration of *N*-allylacetamide, *N,N*-diethylallylamine, and allylbenzene to the respective 1-propenyl derivatives with kinetically controlled *E, Z* isomeric compositions. For the double-bond migration of the latter group of allylic compounds, *π*-coordination of the C=C double bond to $CoHP_3$ was found to occur at the first stage rather than via the nitrogen or oxygen donor-atom. The present study confirmed the utility of pulsed-laser photolysis in observation of time-resolved absorption spectra of transient metal species and in determination of absolute rate constants for coordination, suggesting further application to other organometallic systems.

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17) $CoH[PPh(OEt)_2]_4$; UV_{max} (CH_2Cl_2) 344 nm (ε 6400).

18) In reactions of *N*-allylacetamide with ruthenium(II) and rhodium(I) hydrides, Stille and Becker[11] proposed interaction of the amide oxygen with metal and formation of six-membered metallocycles for dominant production of *Z* isomer.