

The observed energy transfer rate constant (k_{et}^{obs}) depends on the diffusion rate constant (k_{diff}) for diffusion of D^* and A and the energy transfer during the lifetime of the exciplex or complex. If we assume the rate of dissociation of the exciplex or complex to be very fast relative to energy transfer ($k_{-diff} > k_d$)⁴ as in the case of triplet-triplet energy transfer of valerophenone to 2,5-dimethyl-2,4-hexadiene,⁵ the observed rate constant is a composite of the equilibrium constant (k_{diff}/k_{-diff}) for exciplex or complex formation and the rate constant for energy transfer. In this case, the observed energy transfer rate constant is much smaller than the diffusion controlled rate constant. It indicates that the self-quenching of the benzophenone triplets must compete with energy transfer to *trans*-BPYE and the photoisomerization quantum yields decrease as the concentration of benzophenone, $[B]$, increases.

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Rhodium-Olefin Interaction: Double Bond Migration of *cis*-But-2-en-1,4-diol with Rhodium(I) Complexes

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The difference in affinities of rhodium(I) and iridium(I) toward a certain ligand is prominent, e.g., reactions of $\text{IrA}(\text{CO})(\text{PPh}_3)_2$ (A = monodentate anionic ligand such as halogens and ClO_4) with H_2 give stable $\text{Ir}(\text{H})_2\text{A}(\text{CO})(\text{PPh}_3)_2$ which are quantitatively isolated at room temperature¹ while $\text{Rh}(\text{H})_2\text{A}(\text{CO})(\text{PPh}_3)_2$ has never been isolated from the reactions of $\text{RhA}(\text{CO})(\text{PPh}_3)_2$ and H_2 . The M-P bond in $\text{IrCl}(\text{PPh}_3)_3$ is stronger than that in $\text{RhCl}(\text{PPh}_3)_3$; the latter is very effective catalyst for various organic reactions due to the significant dissociation of PPh_3 from rhodium in solution to provide a vacant site around rhodium for organic substrates² while the former is hardly employed as a catalyst mainly because the dissociation of PPh_3 from iridium is negligible.

It has been known that $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ attacks both hydroxyl groups of *cis*- $\text{HOCH}_2\text{CH}=\text{CHCH}_2\text{OH}$ (1) to give *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ but leaves the olefinic group intact.³ The rhodium analogue $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (2), however, behaves quite differently in the reaction with 1, which is described in this report along with related experimental results.

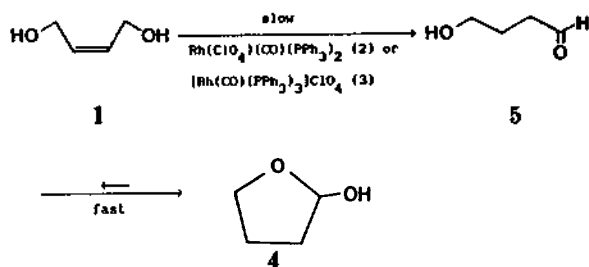
Rhodium-olefinic group interaction is apparent in the reactions of 2 and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (3) with 1 but no evidence for interaction between rhodium (in 2 and 3) and the hydroxyl groups of 1 has been observed (see below). 2-Hydroxytetrahydrofuran (4) is catalytically produced in the reactions of 1 with 2 or 3 (Table 1). Proton NMR spectral changes during the reactions clearly showed that a saturated

Table 1. Catalytic Production of 2-Hydroxytetrahydrofuran (4) in the Reactions of *cis*-But-2-en-1,4-diol (1) (2.0 mmole) with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (2) (0.1 mmole) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (3) (0.1 mmole) at 45 °C under Nitrogen

Catalyst	Solvent	Time, (hr)	Yield (%)
2	$\text{CDCl}_3(0.5 \text{ ml})$	32	100
3	$\text{CDCl}_3(0.5 \text{ ml})$	24	100
2	$\text{CDCl}_3(0.4 \text{ ml}) + \text{CD}_3\text{OD}(0.1 \text{ ml})$	5	100
3	$\text{CDCl}_3(0.4 \text{ ml}) + \text{CD}_3\text{OD}(0.1 \text{ ml})$	3	100
2	$\text{CDCl}_3(0.4 \text{ ml}) + \text{CD}_3\text{COCD}_3(0.1 \text{ ml})$	15	100
3	$\text{CDCl}_3(0.4 \text{ ml}) + \text{CD}_3\text{COCD}_3(0.1 \text{ ml})$	10	100

aldehyde, presumably 4-hydroxybutanal (5), is produced and disappeared when a mixture of CD_3COCD_3 and CDCl_3 is used as a solvent (see Experimental and Table 1). No other products such as but-2-enal (which is produced in the reaction of the iridium complex $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ with 1³) has been found. Accordingly, the production of 4 seems to occur through the formation of 5 (equation 1). Formation of 5 is also strongly supported by the fact that complex 2 and 3 are very effective catalysts for the double bond migration of allylic alcohols to produce the corresponding saturated aldehydes⁴ and the double bond migration product 5 would readily

undergoes cyclization to give 4 in the presence of acid or base and even under neutral conditions.⁵ It should be mentioned that there is no 4-hydroxybutanal (5) left in the reaction mixture at the end of the reaction whereas the equilibrium between 5 and 4 ($5/4 = 11/89$) predicts somewhat significant amount of 5 could be seen.⁵

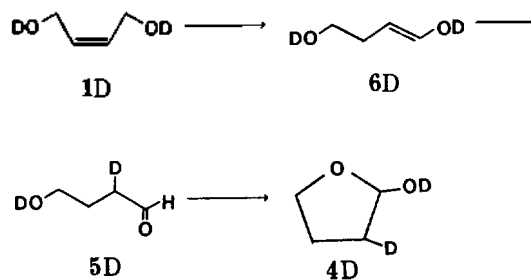


The reaction is slow in CDCl_3 mainly because 1 is not miscible with CDCl_3 and the reaction occurs in a heterogeneous reaction mixture to produce 4 which is miscible with CDCl_3 to give homogeneous solution at the end of the reaction. Addition of CD_3OD or CD_3COCD_3 into CDCl_3 improves the solubility of 1 and makes the reaction rates faster (see Table 1). Slower rates in CD_3COCD_3 than that in CD_3OD is best understood by stronger affinity of CD_3COCD_3 toward rhodium in 2 and 3 than that of CD_3OD ,⁶ i.e., CD_3COCD_3 occupies the coordination site of rhodium more firmly than does CD_3OD , and the former suppresses the interaction of rhodium and the olefinic group of 1 more effectively than does the latter.

Reactions were followed mostly by measuring changes in proton NMR spectra using deuterated solvents. Some experiments, however, were carried out using CH_3OH in place of CD_3OD , and no differences in reaction rates have been found. Exchange between hydroxyl hydrogens of 1 and deuterioxy deuterium of CD_3OD does not seem to affect the rate of the formation of 4. This observation also supports that the double bond migration step (1 \rightarrow 5) is the slow rate determining step and the cyclization step (5 \rightarrow 4) is rather fast step as expected (see text above).

Employing hydroxyl hydrogen deuterated diol, *cis*- $\text{DOCH}_2\text{CH}=\text{CHCH}_2\text{OD}$ (1D) also provides somewhat valuable information on the interactions of 1 with rhodium in 2 and 3. Proton NMR spectrum of the product of the reaction of 1D with 2 (or) unambiguously identifies 2-deuterioxy-3-deuterotetrahydrofuran (4D) as the product which is apparently the cyclization product of 4-deuterioxy-2-deuterobutanol (5D) (equation 2). This observation confirms the interaction between the rhodium and the olefinic group of 1D (and 1) to lead the double bond migration to give a simple enol, 1,4-dideuterioxybut-1-en (6D) which readily undergoes ketonization to produce 5D (equation 2). It has been well-established that a simple enol is generated from the reaction of an allylic alcohol with 2 or 3 and rapidly undergoes ketonization to give the corresponding carbonyl compound in CDCl_3 .⁹ There is no evidence for the interaction between the deuterioxy groups of 1D and the rhodium in 2 or 3 prior to the rhodium-olefinic group interaction. Formation of both 5D (from 6D) and 4D (from 5D) involves O-D bond cleavage, which may not necessarily require the rhodium catalyst (2 or 3) for the following reasons. Ketonization of simple enol is rapid in CDCl_3 in the absence of a metal com-

plex^{9a} and 4-hydroxy aldehyde 5 readily undergoes cyclization to give 5-membered cyclic ether 4 even under neutral conditions.⁵ In short, it may be safely said that the formation of 4 is obtained as the results of the interaction of the olefinic group of 1 with the rhodium in 2 or 3. It still remains, however, obscure why the rhodium in $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ interacts preferably with olefinic group of 1 to initiate the double bond migration while the iridium in $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ attacks OH group of 1 to abstract one of the two OH hydrogens and eventually catalyzes the hydrogenolysis of the other OH group to give $\text{CH}_3\text{CH}=\text{CHCHO}$ and leaves the olefinic group intact.³



Experimental

Materials.

$\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (2) and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (3) were prepared by the literature methods.⁸ *cis*-But-2-en-1,4-diol (1) was purchased from Fluka (19150) and used without further purification. Deuterated diol, *cis*- $\text{DOCH}_2\text{CH}=\text{CHCH}_2\text{OD}$ (1D) was prepared by H-D exchange reaction: a solution of $\text{HOCH}_2\text{CH}=\text{CHCH}_2\text{OH}$ (1, 5 ml) and D_2O (10 ml) was magnetically stirred for 2 hours under nitrogen and treated with MgSO_4 to remove water and filtered. This procedure was repeated further 3 times before it was finally distilled under vacuum to remove the rest of water. Proton NMR spectrum of 1D prepared in this manner showed more than 90% of the OH hydrogens of 1 being replaced with deuteriums.

Catalysis

Reactions in CDCl_3 . A 2.0 mmole of *cis*-but-2-en-1,4-diol (1) was added to a 0.5 ml of CDCl_3 solution of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (2, 0.1 mmole) (or 3) in a 10 ml round bottom flask under nitrogen, and the reactor was kept in a thermostat maintained at 45°C. A 0.5 ml of the reaction mixture was transferred into an NMR tube to analyze the products at intervals. Proton NMR spectra clearly showed that new signals of 2-hydroxytetrahydrofuran (4) ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}$ (OH), δ 1.89 (m); -OH, δ 3.0-5.0 (s); -O- $\text{CH}_2\text{-CH}_2$, δ 3.80 (m); -CH(OH), δ 4.92 (m)) gradually increase at the expense of signals of *cis*-but-2-en-1,4-diol (1) (- CH_2 , δ 4.13 (d); -OH, δ 4.0-6.0 (s); -CH=CH-, δ 5.62 (t)).

Reactions in CDCl_3 and CD_3OD . Addition of CD_3OD (0.1 ml) solution of 1 (2.0 mmole) into CDCl_3 (0.4 ml) of 2 (or 3) under nitrogen yielded a homogeneous yellow solution. A 0.5 ml of the solution was transferred into an NMR tube which was sealed tight with rubber cap and teflon tape and kept in a thermostat maintained at 45°C. Proton NMR spectrum of the reaction mixture was measured at intervals to analyze products.

Reactions in CDCl_3 and CD_3COCD_3 . These reactions

were carried out in the same manner described above for the reactions in CDCl_3 and CD_3OD . In some experiments (but not always) with **2**, a small triplet (with the coupling constant being less than 2 Hz) was observed at $\delta 9.50$ ca. 2 hours after the reaction started and disappeared soon. Appearance and disappearance of this triplet could be observed several times in an experiment. The position, multiplicity and small coupling constant of the triplet unambiguously identify the triplet as the signal due to $-\text{CH}_2-\text{CHO}$.

Reaction with cis-DOCH₂CH=CHCH₂OD (1D) in CDCl_3 and CD_3COCD_3 . This reaction was carried out with **2** in the same manner described above for reactions in CDCl_3 and CD_3COCD_3 . Proton NMR of the final product showed signals only at $\delta 1.89$ (m), 3.80 (m) and 4.92 (m) with integration ratio being 3:2:1 which are in good agreement with **4D**.

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- A CH_3COCH_3 complex, $[\text{Rh}(\text{CH}_3\text{COCH}_3)(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$,⁷ can be isolated in the reactions of CH_3COCH_3 with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**2**) or $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ (**3**) whereas the CH_3OH complex, $[\text{Rh}(\text{CH}_3\text{OH})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ⁸ has never been isolated.
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Structure of Bis(triphenyltin(IV))piperazinebis(dithiocarbamate)

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Structural chemistry of organotin (IV) dithiocarbamate (dtc) complexes has been an interesting subject of study for a long time.¹⁻⁶ However, no accordant evidences are established for the bonding mode of the dtc ligand moiety for triphenyltin(IV) complexes although several physicochemical techniques have been attempted for its characterization.⁷⁻¹¹ Even though the X-ray data determined for a crystalline solid complex gave us decisive evidence on the position of the ligand atoms,^{12,13} they could not be used with certainty for discerning the bonding fashion of the dtc ligand because of its ambiguous bond distance. For further understanding of this system, we report the crystal structure together with the ¹¹⁹Sn NMR of the interesting complex, bis(triphenyltin(IV))piperazinebis(dithiocarbamate), $(\text{Ph}_3\text{SnS}_2\text{CNC}_2\text{H}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2$.

The title complex was prepared by the literature procedure.⁹ Recrystallization of the crude product in a dichloromethane-petroleum ether solvent pair (1:1) at 0°C gave a colorless dichloromethane-solvated crystalline complex suitable for X-ray study. The dichloromethane-solvated crystals were unstable when removed from the mother liquor and, therefore, the crystal used for X-ray study was wedged, wet with mother liquor, into a glass capillary which was then sealed. All the crystallographic data¹⁴ were obtained on an Enraf-Nonius CAD4 diffractometer with graphite mo-

nochromated molybdenum radiation ($\lambda(K_{\alpha 1}) = 0.70930 \text{ \AA}$, $\lambda(K_{\alpha 2}) = 0.71359 \text{ \AA}$) at an ambient temperature of 23(2)°C. The tin atom was located using MULTAN-80,¹⁵ a system of computer program for direct method solution, and the remaining atoms were located in a series of difference Fourier maps and least-squares refinements¹⁶ using SHELX-76.¹⁷ All the hydrogen atoms, carbon atoms of phenyl group, and carbon and chlorine atoms of solvated dichloromethane were refined isotropically. The remaining atoms were refined anisotropically. The carbon atoms of phenyl group were fixed into a regular hexagon. The ¹¹⁹Sn NMR spectrum¹⁸ relative to external Me_4Sn was recorded on a Bruker AM-200 operating at 74.03 MHz (¹¹⁹Sn) in pulse mode with Fourier transform at ambient temperature.

The molecular geometry and labeling scheme along with selected bond distances and angles for the title molecule is shown in Figure 1. The dichloromethane molecules solvated do not interact with the parent molecule and are not shown in the structure. The complex molecule is centrosymmetric. An interesting feature of the structure is the bonding mode of the dtc ligand. The Sn-S(1) distance of 2.473(3) Å is a normal value of Sn-S bond found in typical anisobidentate bonding complexes such as $\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$ (2.497(8) Å)¹⁹ and $(t\text{-Bu})_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$ (2.489(1) Å).²⁰ However, the Sn-S(2) distance of 3.065(3) Å in the present compound is considerably