

# Cyclic acetals from catalytic addition of diols to terminal alkynes with a cationic iridium complex containing two labile ligands

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## Abstract

Cationic iridium complex  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{CO})(\text{OH}_2)(\text{PPh}_3)_2](\text{OTf})$  (**1**) catalyzes addition of diols  $(\text{HO}-(\text{CH}_2)_n-\text{OH})$  ( $n=2-6$ ) to terminal alkynes ( $\text{RC}\equiv\text{CH}$ :  $\text{R}=\text{H}$ ,  $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ) to produce cyclic acetals  $(\text{CH}_3\overset{\text{R}}{\text{C}}(\text{O})(\text{CH}_2)_n\text{O})$  exclusively in the absence of  $\text{H}_2\text{O}$  at room temperature. While complex **1** does not catalyze the hydration of alkynes to produce the carbonyl compounds ( $\text{RCOCH}_3$ ), the cyclic acetals rapidly undergo hydrolysis to give  $\text{RCOCH}_3$  and regenerate diols in the presence of **1**. A deuterium-labeling study ( $\text{MeOD} + n\text{-BuC}\equiv\text{CH} \rightarrow \text{CHD}_2\text{C}(\text{OMe})_2(n\text{-Bu})$ ) suggests a reaction pathway involving a  $\pi$ -alkyne complex,  $\eta^2\text{-(RC}\equiv\text{CH)Ir}$  which is attacked by alcohol ( $\text{R}'\text{OD}$ ) to give a  $\beta$ -alkoxy-alkenyl complex,  $\text{Ir}-\text{CH}=\text{CRO}^+\text{DR}'$ . Proton transfer and attack by another alcohol molecule on the intermediate,  $\text{Ir}-\text{CHD}-\text{C}^+\text{R}(\text{OR}')$  to produce  $\text{Ir}-\text{CHD}-\text{CR}(\text{OR}')-\text{O}^+\text{DR}'$  that finally yields the acetal  $\text{CHD}_2\text{CR}(\text{OR}')_2$ . It has been found that bulky substituents  $\text{R}$  on  $\text{RC}\equiv\text{CH}$  cause a decrease in the rate of diol addition, and that the production of six- and seven-membered acetals is faster than that of five- and eight-membered ones.

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**Keywords:** Iridium; Homogeneous catalysis; Cyclic acetal; Addition of diol; Terminal alkyne

## 1. Introduction

Production of five- and six-membered cyclic acetals is important in the field of mono-saccharides to protect their carbonyl and hydroxyl groups [1]. Aldehydes and ketones could be protected by reactions with 1,2- and 1,3-diols to form five- and six-membered cyclic acetals in the presence of acid catalysts [1,2]. These catalytic reactions should be carried out in the absence of water to suppress the hydrolysis of acetals that regenerates carbonyl compounds. Diols  $(\text{HO}-(\text{CH}_2)_n-\text{OH})$  undergo dehydration reaction to produce cyclic ethers in the presence of acid catalysts [3] and alcohols ( $\text{ROH}$ ) are added to alkynes ( $-\text{C}\equiv\text{C}-$ ) in the presence of acids and even in the presence of bases to give acetals  $(-\text{CH}_2-\text{C}(\text{OR})_2-)$  [4]. Acidic catalysts such as Lewis acid,  $\text{Hg}(\text{II})$  salts, have been used for hydration of alkynes to produce carbonyl compounds [5] whereas transition metal complexes have been lately utilized in the catalytic alcohol

addition to alkynes to produce acetals [6]. Application of these transition metal complexes has shown some advantages such as regio- and stereo-selectivity, over the conventional Lewis acid or base catalysts.

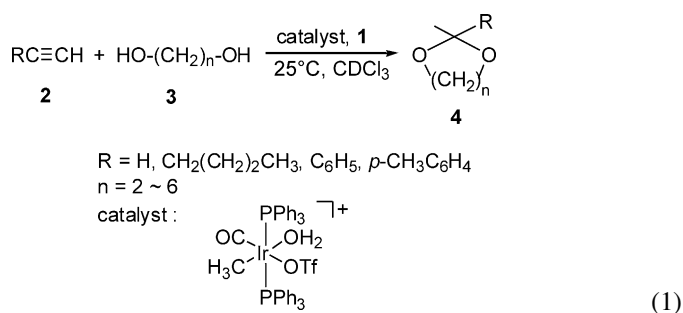
A six-coordinated iridium(III) complex  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{OH}_2)(\text{CO})(\text{PPh}_3)_2](\text{OTf})$  (**1**) is soluble in most alcohols, and the two O-ligands,  $\text{OTf}^-$  and  $\text{H}_2\text{O}$ , of complex **1** are so labile that they can be readily replaced by alkynes and even by alcohols [7]. We recently found that alcohols ( $\text{R}'\text{OH}$ ) are added to the coordinated terminal alkynes ( $\text{RC}\equiv\text{CH}$ ) in the reactions of an iridium complex derived from complex **1** replacing those two labile ligands [8]. These observations prompted us to investigate catalytic activity of complex **1** for the addition of alcohols to alkynes.

We now wish to report a homogeneous catalysis, addition of diols to terminal alkynes to produce cyclic acetals, with the assistance of a cationic iridium complex  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{OH}_2)(\text{CO})(\text{PPh}_3)_2](\text{OTf})$  (**1**). The reaction proceeds under ambient conditions with no water scavenger as long as substrates are water-free. Surprisingly, complex **1** does not catalyze the hydration of alkynes under the same conditions.

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## 2. Results and discussion

Cyclic acetals ( $\text{RC}(\text{CH}_3)\text{-O}(\text{CH}_2)_n\text{O}$ ) are catalytically produced by the addition of diols ( $\text{HO}(\text{CH}_2)_n\text{-OH}$ ,  $n = 2\text{--}6$ ) to terminal alkynes ( $\text{RC}\equiv\text{CH}$ ,  $\text{R}=\text{H}$ ,  $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ) in the presence of **1** at room temperature (Eq. (1)). These reactions (Eq. (1)) do not occur in the presence of  $\text{OTf}^-$  ( $\text{CF}_3\text{SO}_3^-$ ) and in the absence of complex **1**. Accordingly, the reactions are catalyzed by complex **1** but not by  $\text{OTf}^-$  present in the reaction mixture.



The above catalytic reactions (Eq. (1)) of acetylene ( $\text{R}=\text{H}$ ) are fast (see reaction rates in Table 1) with practically no alcohols remaining in the reaction mixture after 2 h. Acetals (**4**) are the sole products in the absence of water whereas considerable amounts of ketones ( $\text{RC}(\text{O})\text{CH}_3$ ) are found whenever small amounts of water are present in the reaction mixture. It should be mentioned that small amounts of ketones are observed in most experiments even when absolute-alcohols (water-free) are used as substrates. These small amounts of ketones are probably the products of the hydration of alkynes by the water coordinated in the catalyst  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{CO})(\text{H}_2\text{O})(\text{PPh}_3)_2]\text{OTf}$ .

Table 1  
Addition of  $\text{HO}(\text{CH}_2)_n\text{-OH}$  ( $n = 2\text{--}6$ ) to  $\text{HC}\equiv\text{CH}$  (1 atm) in the presence of  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{OH}_2)(\text{CO})(\text{PPh}_3)_2](\text{OTf})$  (**1**,  $4.7 \times 10^{-5}$  mol, 6.6 mM) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$  for 10 min

Alcohol	Product	Acetal/Ir (h)
		12.4
		66.8
		50.7
		32.1
		24.8
$\text{CH}_3\text{OH}$		5.23

Diol/Ir = 20;  $\text{HC}\equiv\text{CH}$  is in large excess of diol.

Table 2

Addition of  $\text{HOCH}_2\text{CH}_2\text{OH}$  to  $\text{RC}\equiv\text{CH}$  in the presence of  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{CO})(\text{OH}_2)(\text{PPh}_3)_2](\text{OTf})$  (**1**,  $4.7 \times 10^{-5}$  mol, 6.6 mM) in  $\text{CDCl}_3$  (7 mL) at  $25^\circ\text{C}$  for 3.5 h

$\text{RC}\equiv\text{CH}$	Product	Acetal/Ir (h)
		5.6
		1.3
		0.56

$\text{HOCH}_2\text{CH}_2\text{OH}/\text{RC}\equiv\text{CH}/\text{Ir} = 20/20/1$ .

It is somewhat surprising that production of six- and seven-membered cyclic acetals is significantly faster than that of five-membered ones (see Table 1). The addition reaction of 1,2-ethanediol to hex-1-yne is significantly faster than that to aromatic alkynes (Table 2). Meanwhile, the reaction with  $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$  is faster than that with  $p\text{-CH}_3\text{C}_6\text{H}_4\text{C}\equiv\text{CH}$ . This may be understood from the relative electrophilicity of the  $sp$  carbons ( $\text{RC}\equiv\text{CH}$ ) toward the hydroxyl group of alcohol. The lower rates for these aromatic alkynes than that for  $n\text{-BuC}\equiv\text{CH}$ , however, is not explained simply by relative electrophilicity of the  $sp$  carbons of alkynes ( $\text{RC}\equiv\text{CH}$ ). Both electronic and steric effects should be taken into consideration to understand these results.

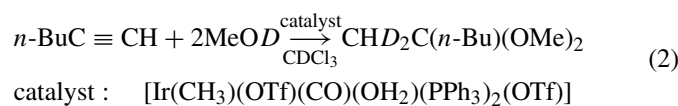
In the presence of complex **1**, the addition of diols to  $\text{HC}\equiv\text{CH}$  to give cyclic acetals (Eq. (1)) is significantly faster than that of methanol (see Table 1). The two OH groups of one diol molecule probably have more chances to interact with one of the carbons of the alkyne coordinated to a metal than two molecules of methanol. Faster rates observed for diols than for methanol (Table 1), accordingly, seem reasonable.

Separate experiments have been carried out to investigate characteristics of these reactions. It is very interesting to find that in the presence of **1**, neither the acetals nor ketones are obtained from the reactions of alkynes (i) with  $\text{H}_2\text{O}$  in the absence of alcohols and (ii) with alcohols in the presence of excess  $\text{H}_2\text{O}$  at room temperature. In the presence of a small amount of  $\text{H}_2\text{O}$ , the alcohol addition (Eq. (1)) takes place at a moderate rate followed by subsequent hydrolysis of the resulting acetals to give ketones ( $\text{RCOCH}_3$ ) and the regenerated alcohols. It has been found in separate experiments that in the presence of complex **1**, those acetals (**4**) rapidly undergo hydrolysis to give the corresponding ketones. These observations may be understood in terms of formation of catalytically inactive species favorable in the presence of excess  $\text{H}_2\text{O}$  where complex **1** undergoes the substitution of its labile ligand ( $\text{OTf}^-$ ) with  $\text{H}_2\text{O}$  to give bis-aqua complex  $[\text{Ir}(\text{CH}_3)(\text{CO})(\text{OH}_2)_2(\text{PPh}_3)_2]^{2+}$ . When this aqua complex is the predominant species in the reaction mixture, one may not expect the catalytic reactions (Eq. (1)) to occur since the catalytic cycle for the reactions (Eq. (1)) must involve metal

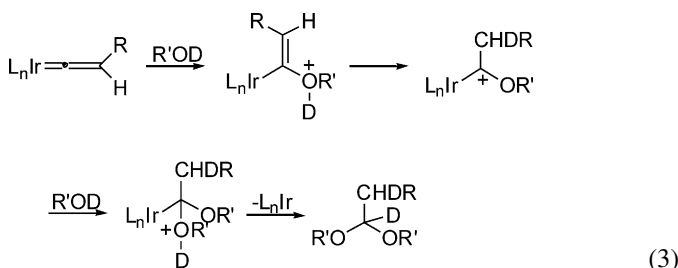
complexes containing coordinated alkynes (see below for the plausible reaction pathway suggested).

It has been known that **1** and related iridium complexes activate alkynes [9]. These iridium complexes react with terminal alkynes ( $\text{RC}\equiv\text{CH}$ ) to give iridium-alkynyls ( $\text{Ir}\equiv\text{R}$ ) and iridium-carbenes ( $\text{M}=\text{C}=\text{CHR}$ ) which show different reactivities [8]. For example, while iridium-alkynyls are readily attacked by electrophiles such as  $\text{H}^+$  or  $\text{Me}^+$  on their  $\beta$ -carbon causing the  $\alpha$ -carbon ( $\text{Ir}-\text{C}^+=\text{CHR}$ ) to be electrophilic for further reactions [9–11], iridium-carbenes readily react with nucleophiles such as  $\text{R}'\text{OH}$  and  $\text{OH}_2$  to form new bonds at the  $\alpha$ -carbon of the carbene ligands with the oxygen of alcohols and water to give metal-alkenyls with the alkoxy group on the  $\alpha$ -carbon,  $\text{Ir}=\text{C}(\text{OR}')\text{CH}_2\text{R}$  [8,10]. On the other hand, many studies suggest mechanisms involving the attack of alcohol ( $\text{R}'\text{OH}$ ) on alkynes while they are coordinated through the  $\pi$ -system ( $\text{M}(\eta^2-\text{RC}\equiv\text{CR}'')$ ) to form metal-alkenyls with the alkoxy group on the  $\beta$ -carbon ( $\text{M}-\text{CR}=\text{CR}'(-\text{OR}')$ ) (see Eq. (4)) [6].

In order to investigate the reaction mechanism for the catalytic addition of alcohol to terminal alkyne (Eq. (1)), deuterium-labeling experiments have been carried out for the reaction of methanol with 1-hexyne. Two deuterium atoms are found only at one carbon of the product (see Eq. (2)). It is certain that the two deuterium atoms are from  $\text{MeOD}$  but not from solvent  $\text{CDCl}_3$  since deuterium has never been observed in the products from the reaction of  $\text{MeOH}$  with  $\text{RC}\equiv\text{CH}$  carried out in  $\text{CDCl}_3$ . It should also be mentioned that only one regio-isomeric product, namely  $\text{CH}_3\text{C}(n\text{-Bu})(\text{OMe})_2$  is observed, and the alternative regio-isomer,  $n\text{-BuCH}_2\text{CH}(\text{OMe})_2$  has never been found in the reaction of  $\text{MeOH}$  and  $n\text{-BuC}\equiv\text{CH}$  in  $\text{CDCl}_3$ .

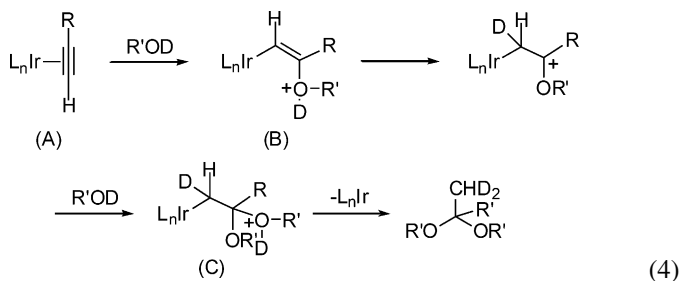


The fact that deuterium is seen only at one carbon of the two  $sp$  carbons of alkynes (Eq. (2)) and that  $\text{CH}_3\text{C}(n\text{-Bu})(\text{OMe})_2$  is the only regio-isomeric product from the reaction of  $\text{MeOH}$  and  $n\text{-BuC}\equiv\text{CH}$  excludes the reaction pathway involving the iridium-carbene ( $\text{Ir}=\text{C}=\text{CHR}$ ) intermediate. One would expect deuterium atoms are expected to be seen at both  $sp$  carbons of the alkyne if the mechanism shown in Eq. (3) [12] works.



Accordingly, the reaction pathway involving  $\eta^2$ -alkyne complex (**A**) and  $\beta$ -alkoxy-alkenyl complex (**B**) seems to be a plausible one to explain the two deuterium atoms at one carbon of the acetal (see Eq. (4)). Ligands such as  $\text{CH}_3$ ,  $\text{CO}$  and  $\text{PPh}_3$  are so firmly coordinated to iridium that they are not readily replaced by alkynes or alcohols [8–11]. The  $\text{L}_n\text{Ir}$  moiety in Eq.

(4) could be either four- or five-coordinate at iridium such as in  $\text{Ir}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$  or  $\text{Ir}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2(\text{L}')$ , respectively, where  $\text{L}'$  may be O-based ligand ( $\text{H}_2\text{O}$ ,  $\text{ROH}$ ,  $\text{OTf}$ ) or alkyne.



The slower rates for the addition of substituted alkynes  $\text{RC}\equiv\text{CH}$  (Table 2) than those for non-substituted alkyne  $\text{HC}\equiv\text{CH}$  (Table 1) may now be understood in terms of relative difficulties for the formation of intermediates (**B**) and (**C**) (Eq. (4)) due to steric effects of crowded  $\text{R}$  and  $\text{R}'$  groups around one carbon.

### 3. Experimental

#### 3.1. Materials

1,3-Propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol 4-ethynyltoluene,  $\text{CDCl}_3$  (from Aldrich), ethyleneglycol (Merck), 1-hexyne (Fluka) and phenylacetylene (Janssen) were reagent grades and used after drying with molecular sieve (type 4A) preheated under vacuum. High purity acetylene was used as purchased from Gyungin Gas Company, Korea.

#### 3.2. Catalyst and products analysis

Catalyst  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{OH}_2)(\text{CO})(\text{PPh}_3)_2](\text{OTf})$  (**1**) was prepared by the literature method (for  $[\text{Ir}(\text{CH}_3)(\text{OCIO}_3)(\text{OH}_2)(\text{CO})(\text{PPh}_3)_2](\text{ClO}_4)$ ) [13] using  $\text{AgOTf}$  instead of  $\text{AgClO}_4$ . Products analysis for catalytic reactions was performed by  $^1\text{H}$  NMR spectral measurements using a Varian Gemini 300 MHz spectrometer.

#### 3.3. Reactions

##### 3.3.1. Catalytic addition of diol to $\text{HC}\equiv\text{CH}$

Diol  $\text{HO}-(\text{CH}_2)_n-\text{OH}$  ( $94 \times 10^{-5}$  mol) was added to a 10 mL of  $\text{CDCl}_3$  solution of complex **1** ( $0.05$  g,  $4.7 \times 10^{-5}$  mol) saturated with  $\text{HC}\equiv\text{CH}$  (1 atm) at  $25^\circ\text{C}$  and the resulting solution stirred for 10 min under 1 atm of  $\text{HC}\equiv\text{CH}$  before a part of the reaction mixture (ca. 0.5 mL) was taken out of the reaction flask for  $^1\text{H}$  NMR measurements to analyze the reaction mixtures.

Reaction of  $\text{OH}-(\text{CH}_2)_2-\text{OH}$  was monitored by integration of the following 300 MHz  $^1\text{H}$  NMR signals in  $\text{CDCl}_3$ :  $\text{CH}_3\text{HCO}(\text{CH}_2)_2\text{O}$  ( $\delta$  5.00, q,  $J=4.8$ ),  $\text{CH}_3\text{CHO}(\text{CH}_2)_2\text{O}$  ( $\delta$  1.38, d,  $J=4.8$ ), and  $\text{HO}(\text{CH}_2)_2\text{OH}$  ( $\delta$  3.70, s).

Reaction of  $\text{OH}-(\text{CH}_2)_3-\text{OH}$ :  $\text{CH}_3\text{HCO}(\text{CH}_2)_3\text{O}$  ( $\delta$  4.61, q,  $J=5.1$ , 1H),  $\text{CH}_3\text{CHO}(\text{CH}_2)_3\text{O}$  ( $\delta$  4.01–3.59, m, 4H),  $\text{CH}_3\text{CHO}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{O}$  ( $\delta$  2.04–1.89, m, 2H),  $\text{CH}_3\text{CHO}(\text{CH}_2)_4\text{O}$  ( $\delta$  1.30, d,  $J=5.1$ , 3H).

Reaction of  $\text{OH}-(\text{CH}_2)_4-\text{OH}$ :  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_4\text{O}}$  ( $\delta$  4.90, q,  $J=5.1$ , 1H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)(\text{CH}_2)_2(\text{CH}_2)\text{O}}$  ( $\delta$  3.90–3.56, m, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)(\text{CH}_2)_2(\text{CH}_2)\text{O}}$  ( $\delta$  1.73–1.65, m, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_4\text{O}}$  ( $\delta$  1.27, d,  $J=5.1$ , 3H). MS  $m/z$  116 ( $\text{MH}^+$ , 1), 115 ( $\text{M}^+$ , 1).

Reaction of  $\text{OH}-(\text{CH}_2)_5-\text{OH}$ :  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_5\text{O}}$  ( $\delta$  4.629, q,  $J=5.4$ , 1H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)(\text{CH}_2)_3(\text{CH}_2)\text{O}}$  ( $\delta$  3.58–3.30, m, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)\text{O}}$  ( $\delta$  1.58–1.45, m, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_2(\text{CH}_2)(\text{CH}_2)_2\text{O}}$  ( $\delta$  1.43–1.36, m, 2H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_5\text{O}}$  ( $\delta$  1.24, d,  $J=5.4$ , 3H).

Reaction of  $\text{OH}-(\text{CH}_2)_6-\text{OH}$ :  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_6\text{O}}$  ( $\delta$  4.63, q,  $J=5.1$ , 1H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)(\text{CH}_2)_4(\text{CH}_2)\text{O}}$  ( $\delta$  3.52–3.35, m, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)(\text{CH}_2)(\text{CH}_2)_2(\text{CH}_2)(\text{CH}_2)\text{O}}$  ( $\delta$  1.54, br, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2\text{O}}$  ( $\delta$  1.36–1.28, m, 4H),  $\text{CH}_3\overline{\text{CHO}(\text{CH}_2)_6\text{O}}$  ( $\delta$  1.270, d,  $J=5.1$ , 3H).

### 3.3.2. Catalytic addition of 1,2-ethandiol to $\text{RC}\equiv\text{CH}$ ( $R = n\text{-butyl}$ , $\text{Ph}$ , $p\text{-tolyl}$ )

Diol  $\text{HOCH}_2\text{CH}_2\text{OH}$  ( $94 \times 10^{-5}$  mol), and  $\text{RC}\equiv\text{CH}$  ( $94 \times 10^{-5}$  mol) were added to a  $\text{CDCl}_3$  solution (10 mL) of complex **1** (0.05 g,  $4.7 \times 10^{-5}$  mol) in a round-bottom flask (50 mL) at 25 °C and resulting solution was stirred for 3.5 h. Reaction mixtures were analyzed in the same manner described above for the reactions of  $\text{HC}\equiv\text{CH}$  with diols by measuring  $^1\text{H}$  NMR signals.  $^1\text{H}$  NMR ( $\delta$ , in  $\text{CDCl}_3$ ):  $\text{CH}_3\overline{\text{RCO}(\text{CH}_2)_2\text{O}}$  ( $\delta$  3.92 for  $R = n\text{-butyl}$ ,  $\delta$  3.94 for  $R = \text{Ph}$ ,  $\delta$  3.94 for  $R = p\text{-tolyl}$ ),  $\text{CH}_3\text{COR}$  ( $\delta$  2.13 for  $R = n\text{-butyl}$ ,  $\delta$  2.61 for  $R = \text{Ph}$ ,  $\delta$  2.58 for  $R = p\text{-tolyl}$ ),  $\text{HO}(\text{CH}_2)_2\text{OH}$  ( $\delta$  3.72 for  $R = n\text{-butyl}$ ,  $\delta$  3.72 for  $R = \text{Ph}$ ,  $\delta$  3.71 for  $R = p\text{-tolyl}$ ).

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