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

Song yi Kim, Chong Shik Chin*, Min-Sik Eum

Department of Chemistry, Sogang University, Seoul 121-742, Republic of Korea

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Abstract

Cationic iridium complex $[Ir(CH_3)(OTf)(CO)(OH_2)(PPh_3)_2](OTf)$ (**1**) catalyzes addition of diols ($HO{-}(CH_2)_n{-}OH$ ($n = 2$–6)) to terminal alkynes ($RC{\equiv}CH$: $R{=}H$, $CH_2(CH_2)_2CH_3$, C_6H_5, p-$CH_3C_6H_4$) to produce cyclic acetals ($CH_3\overline{C(R)O(CH_2)_nO}$) exclusively in the absence of H_2O at room temperature. While complex **1** does not catalyze the hydration of alkynes to produce the carbonyl compounds ($RCOCH_3$), the cyclic acetals rapidly undergo hydrolysis to give $RCOCH_3$ and regenerate diols in the presence of **1**. A deuterium-labeling study ($MeO\boldsymbol{D} + n\text{-}BuC{\equiv}CH \rightarrow CH\boldsymbol{D}_2C(OMe)_2(n\text{-}Bu)$) suggests a reaction pathway involving a π-alkyne complex, η^2-$(RC{\equiv}CH)Ir$ which is attacked by alcohol ($R'O\boldsymbol{D}$) to give a β-alkoxy-alkenyl complex, $Ir{-}CH{=}CRO^+\boldsymbol{D}R'$. Proton transfer and attack by another alcohol molecule on the intermediate, $Ir{-}CH\boldsymbol{D}{-}C^+R(OR')$ to produce $Ir{-}CH\boldsymbol{D}{-}CR(OR'){-}O^+\boldsymbol{D}R'$ that finally yields the acetal $CH\boldsymbol{D}_2CR(OR')_2$. It has been found that bulky substituents R on $RC{\equiv}CH$ 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.

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 ($HO{-}(CH_2)_n{-}OH$) undergo dehydration reaction to produce cyclic ethers in the presence of acid catalysts [3] and alcohols (ROH) are added to alkynes ($-C{\equiv}C-$) in the presence of acids and even in the presence of bases to give acetals ($-CH_2{-}C(OR)_2-$) [4]. Acidic catalysts such as Lewis acid, Hg(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 $[Ir(CH_3)(OTf)(OH_2)(CO)(PPh_3)_2](OTf)$ (**1**) is soluble in most alcohols, and the two O-ligands, OTf^- and H_2O, of complex **1** are so labile that they can be readily replaced by alkynes and even by alcohols [7]. We recently found that alcohols (R′OH) are added to the coordinated terminal alkynes ($RC{\equiv}CH$) 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 $[Ir(CH_3)(OTf)(OH_2)(CO)(PPh_3)_2](OTf)$ (**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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* Corresponding author. Tel.: +82 2 705 8448; fax: +82 2 701 0967.
E-mail address: cschin@sogang.ac.kr (C.S. Chin).

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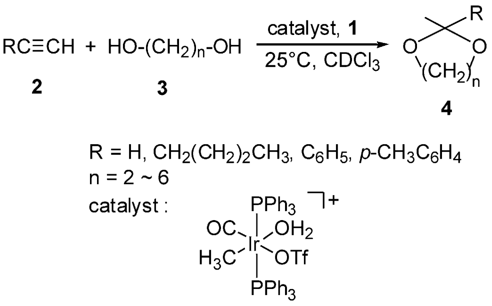
2. Results and discussion

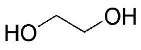
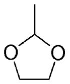
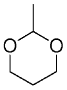
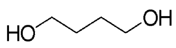
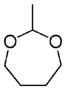
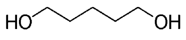
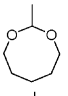
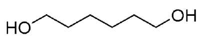
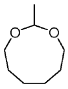
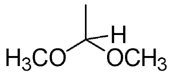
Cyclic acetals $(R\overline{C(CH_3)\text{-}O\text{-}(CH_2)_n\text{-}O})$ are catalytically produced by the addition of diols (HO–$(CH_2)_n$–OH, $n = 2$–6) to terminal alkynes (RC≡CH, R=H, $CH_2(CH_2)_2CH_3$, C_6H_5, p-$CH_3C_6H_4$) in the presence of **1** at room temperature (Eq. (1)). These reactions (Eq. (1)) do not occur in the presence of OTf^- ($CF_3SO_3^-$) and in the absence of complex **1**. Accordingly, the reactions are catalyzed by complex **1** but not by OTf^- present in the reaction mixture.



(1)

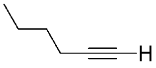
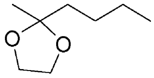
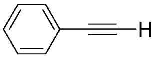
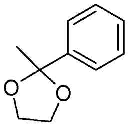
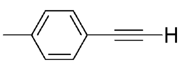
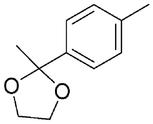
The above catalytic reactions (Eq. (1)) of acetylene (R=H) are fast (see reaction rates in Table 1) with practically no alcohols remaining in the reaction mixture after 2 h. Acetals (**4**) are the sole products in the absence of water whereas considerable amounts of ketones ($RC(O)CH_3$) are found whenever 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 $[Ir(CH_3)(OTf)(CO)(\boldsymbol{H_2O})(PPh_3)_2]OTf$.

Table 1
Addition of HO—$(CH_2)_n$—OH ($n = 2$–6) to HC≡CH (1 atm) in the presence of $[Ir(CH_3)(OTf)(OH_2)(CO)(PPh_3)_2](OTf)$ (**1**, 4.7×10^{-5} mol, 6.6 mM) in $CDCl_3$ at 25 °C for 10 min

Alcohol	Product	Acetal/Ir (h)
		12.4
		66.8
		50.7
		32.1
		24.8
CH_3OH		5.23

Diol/Ir = 20; HC≡CH is in large excess of diol.

Table 2
Addition of $HOCH_2CH_2OH$ to RC≡CH in the presence of $[Ir(CH_3)(OTf)(CO)(OH_2)(PPh_3)_2](OTf)$ (**1**, 4.7×10^{-5} mol, 6.6 mM) in $CDCl_3$ (7 mL) at 25 °C for 3.5 h

RC≡CH	Product	Acetal/Ir (h)
		5.6
		1.3
		0.56

$HOCH_2CH_2OH/RC{\equiv}CH/Ir = 20/20/1$.

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-ethandiol to hex-1-yne is significantly faster than that to aromatic alkynes (Table 2). Meanwhile, the reaction with $C_6H_5C{\equiv}CH$ is faster than that with p-$CH_3C_6H_4C{\equiv}CH$. This may be understood from the relative electrophilicity of the *sp* carbons (R***C***≡CH) toward the hydroxyl group of alcohol. The lower rates for these aromatic alkynes than that for *n*-BuC≡CH, however, is not explained simply by relative electrophilicity of the *sp* carbons of alkynes (R***C***≡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 HC≡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 H_2O in the absence of alcohols and (ii) with alcohols in the presence of excess H_2O at room temperature. In the presence of a small amount of H_2O, the alcohol addition (Eq. (1)) takes place at a moderate rate followed by subsequent hydrolysis of the resulting acetals to give ketones ($RCOCH_3$) 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 H_2O where complex **1** undergoes the substitution of its labile ligand (OTf^-) with H_2O to give bis-aqua complex $[Ir(CH_3)(CO)(OH_2)_2(PPh_3)_2]^{2+}$. 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