Iridium-catalyzed addition of methanol to terminal alkynes

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Abstract

The 18-crown-6 (18C6) ether adduct of sodium hexachloroiridate $[Na(18C6)]_2[IrCl_6]\cdot xH_2O$ (**1**) was found to catalyze an addition of methanol to a variety of nonfunctionalized alkynes $RC\equiv CH$ (R = H, ^nPr, ^nBu, ^nPen, Ph, $HC\equiv C(CH_2)_4$) yielding the corresponding Markovnikov addition products (ketals) and in the cases of hex-1-yne and hept-1-yne also *anti*-Markovnikov ones (acetals, <10%). Furthermore, the reaction of methanol with octa-1,7-diyne resulted in a double Markovnikov addition to only one triple bond, yielding 7,7-dimethoxyoct-1-yne with 80% degree of conversion. On the other hand, the regioselectivity in an addition of methanol to functionalized terminal alkynes of the type $RC(O)C\equiv CH$ (R = OMe, Me) was found to be towards *anti*-Markovnikov products (70–93%). In these two cases vinyl ether intermediates were observed NMR spectroscopically in the course of the reactions.
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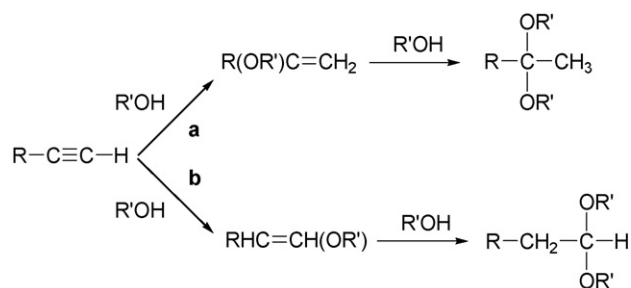*Keywords:* Iridium; Catalysis; Addition of methanol to terminal alkynes; Ketals; Ketones

1. Introduction

A catalytic addition of protic organic substrates $H–YR_n$ (Y, heteroatom; R, alkyl, aryl, H, . . .) to alkynes is a subject of ongoing interest as one of the most efficient routes for a triple bond functionalization. Over the last 80 years many catalytic systems based on Hg [1], Os, Ru, Rh [2], Pd [3], Pt [4], Ag [5] and Au [6] have been reported to catalyze an addition of alcohols to alkynes. However, the reports on iridium-catalyzed addition reactions of protic organic substrates such as alcohols to a triple bond are still very sparse [7]. In 2006 Ishii and co-workers reported an addition of alcohols to non-activated terminal alkynes catalyzed by $[Ir(cod)_2](BF_4)$ in the presence of $P(OR)_3$ (R = Me, Et, iPr) and a Lewis acid ($AlCl_3$, $ZrCl_4$, etc.) [8]. The hydroalkoxylation reactions catalyzed by transition metals have been extensively reviewed [9]. The regioselectivity is an important aspect of such addition reactions. In the case of unsymmetrically disubstituted alkynes, where two addition patterns are principally possible, steric and electronic effects govern the regioselectivity. On the other hand, most of the electrophilic addition reactions of H–Nu (Nu, nucleophile) to terminal alkynes follow the Markovnikov's rule yielding ketals (Scheme 1, **a**), whereas an *anti*-Markovnikov addition is rare and leads to the formation of acetals (Scheme 1, **b**). The regioselectivity in transition metal-catalyzed additions to alkynes may be rationalized in terms of the stability of the competing transition states and intermediate alkyne complexes [10]. The exceptions to Markovnikov's rule include mainly an addition of e.g. alcohols to terminal alkynes $HC\equiv CZ$ bearing a strongly electron-withdrawing group Z such as CHO, COOR, COR, etc. In this case the addition occurs primarily as a nucleophilic attack on the positively charged terminal carbon atom (Michael-type addition) and, as a result, OR group goes to the side away from the Z [11]. The first *anti*-Markovnikov addition of water to terminal alkynes was reported only in 1998 for $RuCl_2/PR_3$ catalytic systems [12]. Much higher activity and perfect selectivity have been achieved later for the cyclopentadienyl ruthenium complexes of the type $[RuCl(Cp)(PR_3)_2]$ and $[RuCl(Cp)(dppm)]$ [13]. However, the reports on the *anti*-Markovnikov addition reactions of other protic substrates, e.g. alcohols to alkynes are still very limited.

Having reported our investigations on the catalytic potential of the 18-crown-6 ether (18C6) adduct of sodium hexachloroiridate $[Na(18C6)]_2[IrCl_6]\cdot xH_2O$ (**1**) in an addition of methanol to internal alkynes [14], we present herein the studies on the addition reactions to terminal alkynes with respect to the Markovnikov/*anti*-Markovnikov regioselectivity.

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Scheme 1.

2. Results and discussion

The 18-crown-6 ether adduct of sodium hexachloroiridate $[Na(18C6)]_2[IrCl_6] \cdot xH_2O$ (**1**) was found to catalyze an addition of methanol to a variety of terminal alkynes. Using 5–10 mol% iridium catalyst **1**, the addition was generally of Markovnikov type (>90%) yielding the corresponding dimethoxyalkanes (ketals) **2a–e** and ketones **2′a–e** as hydrolysis products (Scheme 2). The hydrolysis **2 → 2′** can be catalyzed by the iridium catalyst or/and by traces of HCl in chloroform. The catalytic features and regioselectivities in the addition reactions of methanol to nonfunctionalized terminal alkynes catalyzed by **1** are presented in Table 1. No vinyl ether intermediates were detected NMR spectroscopically in the course of the reactions. Only in the cases of hex-1-yne and hept-1-yne the *anti*-Markovnikov products, **3c/3′c** and **3d/3′d**, respectively, were observed (<10%) (Table 1; entries **c**, **d**). Both addition reactions of methanol to pent-1-yne and phenylacetylene were 100% regioselective and resulted in the formation of Markovnikov products **2b/2′b** and **2e/2′e**, respectively (Table 1; entries **b**, **e**). An addition of methanol as well as of ethanol to acetylene yielded the only possible products, dimethoxy- and diethoxyethane, respectively (Table 1; entries **a**, **a′**). The reaction with methanol was found to be faster than that with ethanol and after 3 h almost a 20-fold excess of acetylene was converted to 1,1-dimethoxyethane (entry **a**). In the addition of ethanol the $n_{alk.}:n_{cat.}$ ratio was found to be more than twice as low after the same reaction time and under the same reaction conditions (entry **a′**). The IR spectrum of the catalyst recovered from the reaction mixture was found to be identical with that for $[Na(18C6)]_2[IrCl_6] \cdot xH_2O$ (**1**). In some cases after a few hours
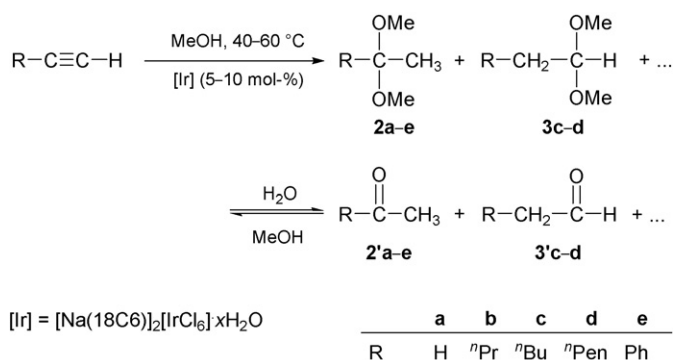
of heating a change of colour of an NMR solution from brown to orange-brown or even to yellow-greenish occurred, indicating presumably a partial reduction of $[IrCl_6]^{2-}$ to $[IrCl_6]^{3-}$. Such reductions in alcoholic media have been known for a long time [15]. However, since the catalytic activity of sodium hexachloroiridate(III) in the addition of methanol to hex-3-yne has also been reported [14], the aforementioned reduction of the catalyst should not affect the activity.

The identities of organic products were confirmed by means of the NMR spectroscopy and the GC/MS measurements without isolation. Thus, running the ^{13}C NMR measurement in the APT mode gave unequivocal proofs for the formation of acetals **3c** and **3d** in the reactions with hex-1-yne and hept-1-yne, respectively. In both cases single resonances at 105.6 ppm were assigned to a tertiary carbon atom of $HC(OMe)_2$ fragment, whereas resonances of a quaternary carbon atom for ketals **2c** and **2d** were found at 102.4 ppm. In the MS spectra of acetals a base peak at m/z 75 corresponds to $HC(OMe)_2$, whereas the base peaks of ketals correspond to the loss of an alkyl chain. Mass spectrometry excluded also the formation of aldehyde cyclotrimerization products, 1,3,5-trioxanes.

In the addition of CD_3OD to hex-1-yne a H/D exchange of protons was also observed (Scheme 3). The H/D exchange catalyzed by **1** was found to proceed only at the positions activated by a neighbored ketal or ketone function, resulting in the formation of two partially deuterated products, **2c(D)** and **3c(D)**, the latter one being observed in the GC/MS spectrum (<5%). However, the terminal hydrogen atom in **3c(D)** was not exchanged. A degree of deuteration was calculated from MS isotopic pattern to be ca. 98%. Since an enol, a ketal and a keto form remain in ketoenol and ketal-ketone equilibria, the H/D exchange catalyzed by **1** presumably takes place at those stages. Such a H/D exchange is not unusual for iridium and has been recently reported by Bergman et al. for $[IrCl_2Cp^*(PMe_3)]$ [16].

The addition of methanol to octa-1,7-diyne catalyzed by **1** (Table 1; entry **f**) resulted, unexpectedly, in a double Markovnikov addition to only one triple bond, yielding after 5 days one product, 7,7-dimethoxyoct-1-yne (**2f**) with 80% degree of conversion (Scheme 4). Upon addition of water the ketal was quantitatively hydrolyzed to oct-7-yn-2-one (**2′f**). Longer reaction time resulted in the formation of other unidentified products. Despite the fact that the titanium-catalyzed synthesis of oct-7-yn-2-one from octa-1,7-diyne has been already reported [17], there has been no evidence on preparation and characterization of 7,7-dimethoxyoct-1-yne so far. The identities of both products were confirmed by means of the NMR spectroscopy. Thus, in the case of **2f** the resonances at 68.1 and 83.9 ppm in the ^{13}C NMR spectrum were assigned, respectively, to the H–C≡ and ≡C–C fragments, whereas a single resonance of the quaternary carbon atom was found at 101.5 ppm. The ^1H NMR spectrum supported the identity of **2f**, showing a single resonance at 1.11 ppm and a triplet at 1.83 ppm that were assigned to the methyl group and the H–C≡ fragment, respectively.

An addition of methanol to functionalized terminal alkynes catalyzed by **1** has been investigated using methyl propiolate, but-3-yn-2-one and ethoxyacetylene (Table 1; entries **g–i**). Using 5 mol% iridium catalyst, methyl propiolate

Scheme 2.

Table 1
Catalytic features and regioselectivities in an addition of methanol to terminal alkynes RC≡CH catalyzed by $[Na(18C6)]_2[IrCl_6] \cdot xH_2O$ (**1**)

| Entry	R	$n_{alk.}:n_{cat.}$	T (°C)	t (h)	Degree of conversion (%)[a]	**2/2′:3/3′** (%)[a]
a	H	18:1	40	3	100	
a′[b]	H	7:1	40	3	100	
b	^{n}Pr	20:1	60[c]	96	100	100:0
c	^{n}Bu	20:1	60	72	100	>95:<5
d	^{n}Pen	10:1	45	96	68	
				216	95[d]	>90:<10
e	Ph	10:1	60	72	100	100:0
	Ph	10:1	45	24	22	
				48	40	
				144	95	100:0
f	HC≡C(CH₂)₄	25:1	45	24	30	
				96	61	
				120	80	100:0
g	MeOC(O)	20:1	45	72	100	20–30:70–80
		10:1	60	24	100	20–25:75–80
h	MeC(O)	20:1	45	96	100	7–11:89–93
I	OEt	17:1	25	2	100	100:0

[a] Determined by NMR spectroscopy, 0–10% of by-products.
[b] Using EtOH instead of MeOH.
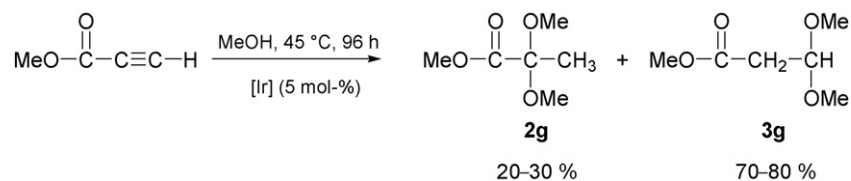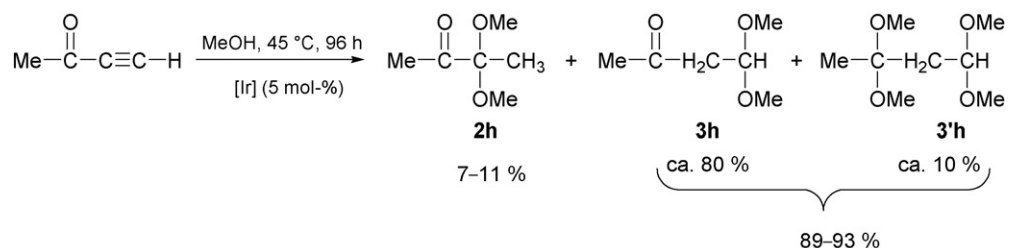[c] First 48 h at 45 °C.
[d] 10–15% of by-products.
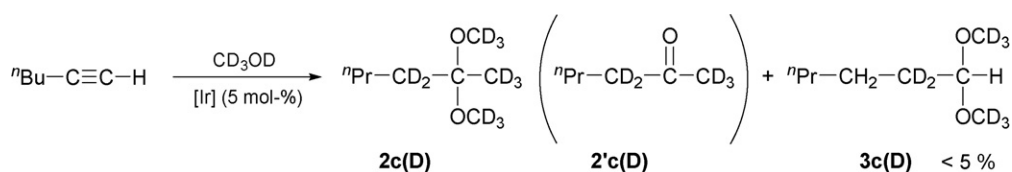
Scheme 3.
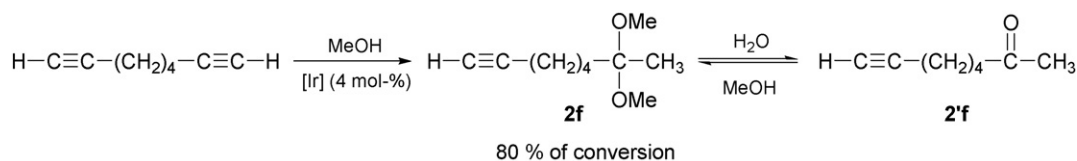
Scheme 4.

Scheme 5.

Scheme 6.

was converted into the corresponding *anti*-Markovnikov product, methyl 3,3-dimethoxypropanoate (**3g**) and methyl 2,2-dimethoxypropanoate (**2g**) (**2g**:**3g** = 20–30%:70–80%) (Scheme 5). Similarly, the analogous addition of methanol to but-3-yn-2-one was found to be generally regioselective (89–93%) towards the *anti*-Markovnikov addition products, yielding 4,4-dimethoxybutan-2-one (**3h**) (ca. 80%) and also 1,1,3,3-tetramethoxybutane (**3′h**) (ca. 10%) (Scheme 6). In this case 7–11% of the corresponding Markovnikov addition product, 3,3-dimethoxybutan-2-one (**2h**) was also observed. Both addition reactions were found to proceed via the intermediate vinyl ethers RHC=CH(OMe), methyl *trans*-3-methoxyacrylate (R = CO$_2$Me, **3g(v)**) and *trans*-4-methoxybut-3-en-2-one (R = C(O)Me, **3h(v)**), respectively, which were observed in the NMR solutions. Thus, a single resonance at 107.0 (R = C(O)Me) or 95.7 ppm (R = CO$_2$Me) in the ^{13}C NMR spectrum can be assigned to the H–C= fragment, whereas the low-field shifted resonances at 165.2 ppm to the =CH(OMe) fragment. In the ^{1}H NMR spectrum the corresponding proton resonances of the H–C= fragments can be found as doublets in the region typical for olefins at 5.13 (**3g(v)**) and 5.53 ppm (**3h(v)**). Similarly, both proton resonances of the =CH(OMe) fragments are low-field shifted and appear as doublets at 7.30 (**3g(v)**) and 7.60 ppm (**3h(v)**). Spectroscopic data for both vinyl ethers are consistent with those in the integrated spectral database system for organic compounds (SDBD) [18]. In both aforementioned reactions with terminal alkynes RC≡CH (R = CO$_2$Me, C(O)Me) the methoxy groups tend to go to the side away from an electron-withdrawing substituent R. The addition occurs as a nucleophilic attack on the positively charged terminal carbon atom to yield predominantly the *anti*–Markovnikov products **3g** and **3h/3′h**. However, in both additions the classical Markovnikov products **2g** and **2h** are also formed, resulting from an attack on the C atom next to the C=O group.

Upon addition of methanol to ethoxyacetylene at room temperature the formation of 1,1,1-trimethoxyethane (**2i**) and its hydrolysis products (methyl acetate (**2′i**) and ethanol) was observed (Scheme 7). Traces of 1,1-dimethoxy–1–ethoxyethane and ethyl acetate were also detected NMR spectroscopically. Since the reaction was carried out in methanol, an exchange of the ethyl group for the methyl one (transesterification) was observed. Furthermore, a test reaction revealed that the addition
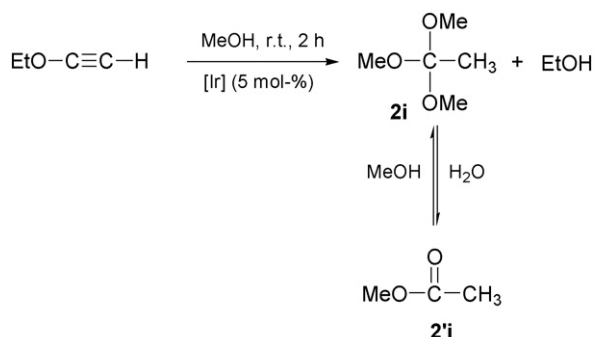
of methanol to ethoxyacetylene took place also in the absence of **1** but in considerably longer reaction time (96 h versus 2 h). This finding is, however, not surprising since an addition of water to acetylenic ethers has been reported to proceed without a catalyst with the formation of carboxylic esters [11]. The reactions with ethoxyacetylene and acetylene were found to be much faster than with other terminal alkynes. The observed differences in reaction rates may be rationalized in terms of the stability of intermediate alkyne complexes.

Our results show that the 18–crown–6 ether adduct of sodium hexachloroiridate [Na(18C6)]$_2$[IrCl$_6$]·xH$_2$O (**1**) is also capable of catalyzing an addition of methanol to diverse terminal alkynes. In the case of alkyl– and aryl–substituted alkynes products are predominantly of Markovnikov type, whereas for terminal alkynes with an electron–withdrawing substituent the *anti*–Markovnikov regioselectivity has been observed.

3. Experimental

All reactions and manipulations were carried out under argon using standard Schlenk techniques. Deuterated water–free solvents (CD$_3$OD, CDCl$_3$, CD$_2$Cl$_2$) were used as received. Methanol was dried over Mg and distilled from NaBH$_4$/Na$_2$[Fe(pc)]·5.5THF (H$_2$pc = phthalocyanine). [Na(18C6)]$_2$[IrCl$_6$]·xH$_2$O (**1**) was synthesized according to the procedure described elsewhere [14]. All alkynes were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200, VXR 400 and Unity 500 spectrometers. Chemical shifts are relative to C*H*Cl$_3$ (δ 7.24), C*H*DCl$_2$ (δ 5.32), C*H*D$_2$OD (δ 3.30) and *C*DCl$_3$ (δ 77.0), *C*D$_2$Cl$_2$ (δ 53.8), *C*D$_3$OD (δ 49.0) as internal references. Assignment of NMR signals, if necessary, was revealed with a help of the ^{13}C APT and HSQC NMR experiments. GC/MS analyses were carried out using a Hewlett Packard (GC HP 5890 Series II, MS HP 5972) spectrometer equipped with a mass selective detector (70 eV).

3.1. Catalytic reactions

In a Schlenk tube [Na(18C6)]$_2$[IrCl$_6$]·xH$_2$O (**1**) (0.020–0.031 mmol) was dissolved in a CD$_2$Cl$_2$/CH$_3$OH or CDCl$_3$/CH$_3$OH solution (0.8–1 ml, less than 40 vol.% of CD$_2$Cl$_2$ or CDCl$_3$). An alkyne (n_{alkyne}:$n_{catalyst}$ = 10:1–20:1) was then added by means of a syringe. The reaction mixture was transferred under argon to an NMR tube that was evacuated and sealed by melting. The reaction mixture was heated at 40–60 °C. In the case of acetylene it was passed through a solution of **1** in a corresponding alcohol for 3 h at 40 °C. In appropriate time intervals ^{1}H and ^{13}C NMR spectra were recorded to monitor the course of the reactions. Upon completion of the reactions ketals were hydrolyzed quantitatively to ketones. The identities of products were confirmed by comparison of their ^{1}H and ^{13}C NMR spectra with those of authentic samples or available in literature, in integrated spectral database SDBD [18] as well as by means of GC/MS measurements. In the reactions with hex–1–yne and hept–1–yne the ^{1}H NMR resonances of acetals were of low intensities and overlapped with those of ketals.

Scheme 7.

Due to that the amount of *anti*–Markovnikov products in these two cases was estimated on a basis of an intensity ratio for a tertiary carbon atom of an acetal and a quaternary one of a ketal in the ^{13}C NMR spectrum.

3.2. Spectroscopic data of selected ketals/acetals and vinyl ethers

3.2.1. 1,1–Dimethoxyethane (2a)
^{13}C NMR (CDCl$_3$/CH$_3$OH, 100.6 MHz): δ 18.3 (*C*H$_3$C), 52.1 (O*C*H$_3$), 101.0 (H*C*(OCH$_3$)$_2$). ^{1}H NMR (CDCl$_3$/CH$_3$OH, 400 MHz): δ 1.08 (d, 3H, ^3J(H,H) = 5.3 Hz, C*H*$_3$CH), 3.12 (s, 6H, OC*H*$_3$), 4.36 (q, 1H, ^3J(H,H) = 5.3 Hz, CH$_3$C*H*).

3.2.2. 1,1–Diethoxyethane (2a′)
^{13}C NMR (CDCl$_3$/CH$_3$OH, 100.6 MHz): δ 15.0 (*C*H$_3$CH$_2$), 19.6 (*C*H$_3$C), 60.5 (O*C*H$_2$), 99.2 (H*C*(OCH$_3$)$_2$). ^{1}H NMR (CDCl$_3$/CH$_3$OH, 400 MHz): δ 1.14 (d, 3H, ^3J(H,H) = 5.4 Hz, C*H*$_3$CH), 3.30–3.37 (m, 2H, OC*H*$_A$*H*$_B$), 4.52 (q, 1H, ^3J(H,H) = 5.4 Hz, CH$_3$C*H*), one C*H*$_3$ resonance overlapped with that of EtOH.

3.2.3. 7,7–Dimethoxyoct–1–yne (2f)
^{13}C NMR (CDCl$_3$/CH$_3$OH, 100.6 MHz): δ 18.0 (*C*H$_2$C≡), 20.5 (*C*H$_3$), 23.0 (*C*H$_2$), 28.3 (*C*H$_2$), 35.6 (*C*H$_2$C), 47.6 (O*C*H$_3$), 68.1 (H*C*≡C), 83.9 (HC≡*C*), 101.5 (*C*(OCH$_3$)$_2$). ^{1}H NMR (CDCl$_3$/CH$_3$OH, 400 MHz): δ 1.11 (s, 3H, C*H*$_3$), 1.83 (t, 1H, *H*C≡, overlapped with that resonance of octa–1,7–diyne), 3.01 (s, 6H, OC*H*$_3$). The C*H*$_2$ resonances could not be unequivocally assigned.

3.2.4. Methyl 2,2–dimethoxypropanoate (2g)
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 20.8 (*C*H$_3$), 49.7 (O*C*H$_3$), 52.4 (C(O)O*C*H$_3$), 100.6 (*C*(OCH$_3$)$_2$), 171.0 (*C*=O). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 1.34 (s, 3H, C*H*$_3$), 3.10 (s, 6H, OC*H*$_3$), 3.64 (s, 3H, C(O)OC*H*$_3$). MS (rel. int. %): m/z = 117 (24) [M–OCH$_3$]$^+$, 89 (100) [CH$_3$C(OCH$_3$)$_2$]$^+$, 85 (10), 57 (16), 47 (11), 43 (85) [CH$_3$C≡O:]$^+$.

3.2.5. Methyl 3,3–dimethoxypropanoate (3g)
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 39.1 (*C*H$_2$), 51.6 (C(O)O*C*H$_3$), 53.6 (O*C*H$_3$), 102.2 (H*C*(OCH$_3$)$_2$), 171.1 (*C*=O). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 2.50 (d, 2H, ^3J(H,H) = 6.0 Hz, C*H*$_2$CH), 3.54 (s, 3H, C(O)OC*H*$_3$), 4.65 (t, 1H, ^3J(H,H) = 6.0 Hz, CH$_2$C*H*), OC*H*$_3$ resonance could not be assigned due to overlapping with that of MeOH. MS (rel. int. %): m/z = 133 (7) [M–CH$_3$]$^+$, 117 (14) [M–OCH$_3$]$^+$, 75 (100) [HC(OCH$_3$)$_2$]$^+$, 59 (13), 47 (18), 43 (13).

3.2.6. Methyl trans–3–methoxyacrylate (3g(v))
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 51.2 (C(O)O*C*H$_3$), 57.7 (O*C*H$_3$), 95.7 (C(O)*C*H=), 165.2 (=*C*H(OCH$_3$)), 169.2 (*C*=O). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 3.58 (s, 3H, OC*H*$_3$), 3.61 (s, 3H, C(O)OC*H*$_3$), 5.13 (d, 1H, ^3J(H,H) = 12.6 Hz, *H*C=), 7.30 (d, 1H, ^3J(H,H) = 12.6 Hz, =C*H*(OCH$_3$)).

3.2.7. 3,3–Dimethoxybutan–2–one (2h)
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 19.5 (*C*H$_3$C), 25.9 (*C*H$_3$C(O)), 48.0 (O*C*H$_3$), 103.0 (*C*(OCH$_3$)$_2$), 207.7 (*C*=O). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 1.24 (s, 3H, C*H*$_3$), 2.11 (s, 2H, C*H*$_2$), 3.06 (s, 6H, OC*H*$_3$). MS (rel. int. %): m/z = 101 (33) [M–OCH$_3$]$^+$, 89 (70) [CH$_3$C(OCH$_3$)$_2$]$^+$, 73 (22), 47 (8), 43 (100) [CH$_3$C≡O:]$^+$.

3.2.8. 4,4–Dimethoxybutan–2–one (3h)
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 30.6 (*C*H$_3$), 47.5 (*C*H$_2$), 53.7 (O*C*H$_3$), 102.1 (H*C*(OCH$_3$)$_2$), 207.0 (*C*=O). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 2.06 (s, 3H, C*H*$_3$), 2.65 (d, 2H, ^3J(H,H) = 5.6 Hz, C*H*$_2$CH), 4.66 (t, 1H, ^3J(H,H) = 5.6 Hz, CH$_2$C*H*), OC*H*$_3$ resonance could not be assigned due to overlapping with that of MeOH. MS (rel. int. %): m/z = 117 (13) [M–CH$_3$]$^+$, 101 (12) [M–OCH$_3$]$^+$, 85 (10), 75 (60) [HC(OCH$_3$)$_2$]$^+$, 47 (13), 43 (100) [CH$_3$C≡O:]$^+$.

3.2.9. 1,1,3,3–Tetramethoxybutane (3′h)
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 21.6 (*C*H$_3$), 40.4 (*C*H$_2$), 52.8 (O*C*H$_3$), 100.8 (*C*(OCH$_3$)$_2$), 102.7 (H*C*(OCH$_3$)$_2$). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 1.19 (s, 3H, C*H*$_3$), 1.82 (d, 2H, ^3J(H,H) = 4.8 Hz, C*H*$_2$CH), 4.38 (t, 1H, ^3J(H,H) = 4.9 Hz, CH$_2$C*H*), OC*H*$_3$ resonance could not be assigned due to overlapping with that of MeOH. MS (rel. int. %): m/z = 89 (40) [CH$_3$C(OCH$_3$)$_2$]$^+$, 75 (100) [HC(OCH$_3$)$_2$]$^+$, 47 (10), 43 (20).

3.2.10. trans–4–Methoxybut–3–en–2–one (3h(v))
^{13}C NMR (CD$_2$Cl$_2$/CH$_3$OH, 100.6 MHz): δ 27.1 (*C*H$_3$), 58.0 (O*C*H$_3$), 107.0 (C(O)H*C*=), 165.2 (=*C*H(OCH$_3$)), 199.6 (*C*=O). ^{1}H NMR (CD$_2$Cl$_2$/CH$_3$OH, 400 MHz): δ 2.17 (s, 3H, C*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 5.53 (d, 1H, ^3J(H,H) = 12.8 Hz, *H*C=), 7.60 (d, 1H, ^3J(H,H) = 12.8 Hz, =C*H*(OCH$_3$)).

3.3. Selected spectroscopic data of deuterated ketals/acetals

3.3.1. ^{n}PrCD$_2$C(OCD$_3$)$_2$CD$_3$ (2c(D))
^{13}C NMR (CD$_3$OD, 125.7 MHz): δ 12.9 (*C*H$_3$CH$_2$), 19.0 (m, *C*D$_3$), 22.5 (*C*H$_2$CH$_2$), 25.8 (*C*H$_2$CD$_2$), 35.0 (qn, *C*D$_2$C), 101.4 (*C*(OCD$_3$)$_2$), O*C*D$_3$ resonance overlapped with that of CD$_3$OD. MS (rel. int. %): m/z = 139 (6) [M–CD$_3$]$^+$, 123 (38) [M–OCD$_3$]$^+$, 98 (100) [M–CH$_3$(CH$_2$)$_2$CD$_2$]$^+$.

3.3.2. ^{n}BuCD$_2$CH(OCD$_3$)$_2$ (2′c(D))
MS (rel. int. %): m/z = 120 (9) [M–OCD$_3$]$^+$, 81 (100) [HC(OCD$_3$)$_2$]$^+$.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.01.001.

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