

# Iridium-catalyzed addition of methanol to internal alkynes

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## Abstract

The 18-crown-6 (18C6) ether adduct of sodium hexachloroiridate  $[\text{Na}(18\text{C}6)]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  (**1**) was found to catalyze an addition of methanol to a wide variety of internal alkynes  $\text{RC}\equiv\text{CR}'$  ( $\text{R/R}' = \text{Et/Et}, \text{Me/Et}, \text{Me}/n\text{Pr}, \text{Me}/n\text{Bu}, \text{Me}/t\text{Bu}, \text{Me}/\text{Ph}, \text{Et}/n\text{Pr}, \text{Et}/\text{Ph}$ ) yielding the corresponding ketals and, due to the presence of water traces, their hydrolysis products (ketones). The regioselectivity of the addition of methanol to unsymmetrically disubstituted internal alkynes is governed by steric and electronic factors, being the highest in the case of pent-2-yne, hex-2-yne and hept-2-yne (80–85%). In the case of  $\text{MeC}\equiv\text{CCO}_2\text{Me}$ , an alkyne having an electron-withdrawing substituent, the addition was found to be 100% regioselective, with two methoxy groups going to the side away from an ester group. Furthermore, in the analogous addition of methanol to  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ , besides the vinyl ethers (*E*)/(*Z*)- $\text{MeO}_2\text{CC}(\text{OMe})=\text{CHCO}_2\text{Me}$ , a cyclotrimerization product ( $\text{C}_6(\text{CO}_2\text{Me})_6$ ) was also observed. A comparison of the catalytic potential of other iridium compounds in the addition of methanol to hex-3-yne revealed that all examined ionic hexachloroiridates ( $[\text{Na}(18\text{C}6)]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$ ,  $\text{Na}_2[\text{IrCl}_6] \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_2[\text{IrCl}_6] \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_3[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$ ) were catalytically active, whereas  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  and  $[\text{IrCl}_2\text{Cp}^*]_2$  were found to be almost inactive (degree of conversion <10%). However, the best results were obtained for the crown ether adduct **1**. Moreover, in the addition of  $\text{CD}_3\text{OD}$  to hex-3-yne,  $[\text{Na}(18\text{C}6)]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  (**1**) was also found to catalyze a H/D exchange of protons in the neighborhood of a keto group or a quaternary carbon of a ketal with a degree of deuteration >97%.

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**Keywords:** Iridium; Catalysis; Addition of methanol to alkynes; Ketals; Ketones

## 1. Introduction

Over 40 years after Reppe's work on the transition metal-catalyzed reactions of acetylenes, in the last two decades a "renaissance" of alkynes chemistry has been observed. A special attention has been paid to a catalytic addition of protic organic substrates  $\text{H}-\text{YR}_n$  ( $\text{Y}$ : heteroatom;  $\text{R}$ : alkyl, aryl,  $\text{H}$ , ...) to alkynes as one of the most efficient routes for their functionalization. Only in 1923 Nieuwland et al. [1] found that a  $\text{Hg}(\text{II})/\text{H}^+$  system catalyzed an addition of alcohols to alkynes yielding acetals. Since that time many other catalytic systems based on  $\text{Hg}$  [2],  $\text{Os}$ ,  $\text{Ru}$ ,  $\text{Rh}$  [3],  $\text{Pt}$  [4],  $\text{Ag}$  [5],  $\text{Au}$  [6] and so on [7] have been reported to catalyze hydroalkoxylation of alkynes. However, there are only a few reports on an iridium-catalyzed addition of protic organic substrates e.g. alcohols to a triple bond. In 2006, Ishii et al. reported an addition of alcohols to non-activated terminal alkynes catalyzed by  $[\text{Ir}(\text{cod})_2](\text{BF}_4)$

in the presence of  $\text{P}(\text{OR})_3$  ( $\text{R} = \text{Me}, \text{Et}, i\text{Pr}$ ) and a Lewis acid ( $\text{AlCl}_3$ ,  $\text{ZrCl}_4$ , etc.) [8]. Furthermore, in the iridium-containing system, which utilizes triangular heterobimetallic sulfido clusters  $[(\text{Cp}^*\text{Ir})_2(\mu_3\text{-S})_2\text{MCl}_2]$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) as precatalysts, the catalysis is believed to proceed on the platinum/palladium center with a minor role of iridium [9]. Recently, an addition of diols to terminal alkynes catalyzed by  $[\text{Ir}(\text{CH}_3)(\text{OTf})(\text{CO})(\text{OH}_2)](\text{PPh}_3)_2(\text{OTf})$  to produce cyclic acetals has also been reported [10].

The investigations on the catalytic potential of tetra- and hexachloroplatinate as well as of tetrachloropalladate complexes in an addition of alcohols to acetylene, carried out in our group, have shown the high activity of platinum salts and, surprisingly, very low activity of palladium compounds [4a–b]. In spite of several catalytic applications of analogous hexachloroiridate(IV) complexes  $[\text{IrCl}_6]^{2-}$  in oxidation reactions [11], such complexes have not been investigated in a catalytic addition of nucleophiles to alkynes so far. Moreover, despite the apparent simplicity of addition reactions to alkenes and alkynes, it is still an important challenge to control the regioselectivity of such processes.

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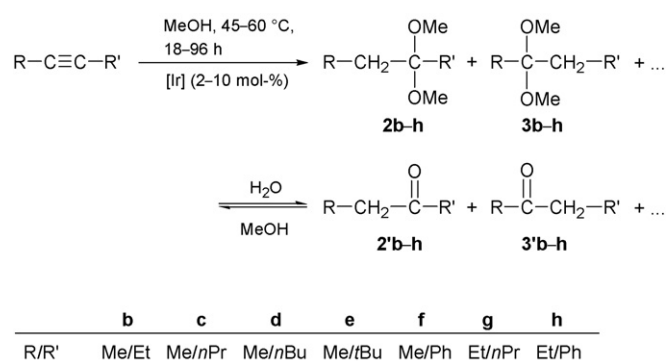
Here we report an addition of methanol to a variety of internal alkynes catalyzed by the 18-crown-6 ether (18C6) adduct of sodium hexachloroiridate  $[\text{Na}(18\text{C}6)]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  (**1**).

## 2. Results and discussion

The 18-crown-6 ether adduct of sodium hexachloroiridate  $[\text{Na}(18\text{C}6)]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  (**1**) was prepared in the reaction of  $\text{Na}_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  with 18-crown-6 ether in methylene chloride as an orange-red to orange-brown powder in very good yield up to 85%. In contrast to the starting material, it shows remarkably better solubility in water and organic solvents (well soluble in methanol, ethanol and acetone, sparingly soluble in chlorinated solvents). Compound **1** melts with decomposition at 191–194 °C. The content of solvated water was calculated on the basis of thermogravimetric analysis to be in the range 0.5–3.0 for different batches. The IR spectrum of **1** revealed a band at  $310\text{ cm}^{-1}$  that was assigned to the Ir–Cl stretching vibration. This band is shifted to a lower wave number in comparison with  $\text{Na}_2[\text{IrCl}_6]$  ( $319\text{ cm}^{-1}$ ).

$[\text{Na}(18\text{C}6)]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  (**1**) was found to catalyze an addition of methanol to a variety of disubstituted internal alkynes, resulting in the formation of the corresponding dimethoxyalkanes (ketals) and, due to the presence of water traces, also their hydrolysis products (ketones). Using 2 mol% iridium catalyst **1**, the addition of methanol to hex-3-yne yielded 3,3-dimethoxyhexane (**2a**) and hexan-3-one (**2'a**) ( $2\mathbf{a} + 2'\mathbf{a} > 90\%$ ,  $2\mathbf{a}/2'\mathbf{a} = 65\text{--}95/5\text{--}35\%$ ) (Scheme 1, **a**). No vinyl ether intermediate was detected NMR spectroscopically in the course of the reaction. Furthermore, a control experiment revealed that the addition of methanol to hex-3-yne did not proceed without the iridium catalyst. The hydrolysis  $2\mathbf{a} \rightarrow 2'\mathbf{a}$  can be catalyzed by the iridium catalyst or/and by traces of HCl in chloroform. Tertiary alcohols were inactive as no products were observed in the reaction of hex-3-yne with *tert*-butanol in nitromethane after several days. The addition of methanol to diphenylacetylene catalyzed by **1** failed, presumably, due to steric effects of two phenyl rings. However, other catalytic systems such as  $\text{Hg}(\text{OAc})_2/\text{H}^+$  [2g] or  $[\text{Au}(\text{PR}_3)]^+$  (R = alkyl, aryl) [6a] were found to catalyze efficiently the addition of methanol also to diphenylacetylene.

When the addition of  $\text{CD}_3\text{OD}$  to hex-3-yne was carried out, a H/D exchange of protons was observed (Scheme 1, **b**). The H/D exchange catalyzed by **1** was found to proceed only at the posi-

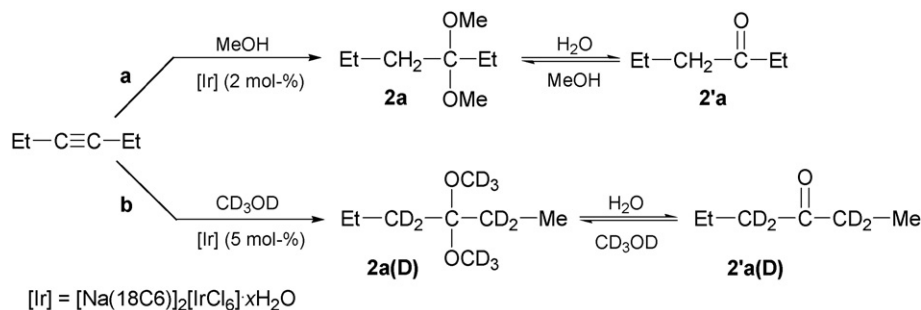


Scheme 2.

tions activated by a neighbored ketal or ketone function, resulting in the formation of two partially deuterated products, **2a(D)** and **2'a(D)**. A degree of deuteration was calculated from MS isotopic pattern to be ca. 97%. Such a H/D exchange is commonly catalyzed by a variety of transition metals and has been recently reported also for iridium complexes, e.g.  $[\text{IrCl}_2\text{Cp}^*(\text{PMe}_3)]$  that was found to catalyze efficiently low temperature H/D exchange between  $\text{D}_2\text{O}$  or  $\text{C}_6\text{D}_6$  and various organic substrates without added acids or stabilizers [12]. Since a ketal, a ketone and an enol form remain in an equilibrium, the H/D exchange catalyzed by **1** presumably takes place at those stages.

In the case of unsymmetrically substituted alkynes  $\text{RC}\equiv\text{CR}'$  two addition patterns are possible and, indeed, a reaction with methanol in the presence of **1** resulted in the formation of two ketals **2b-h** and **3b-h** as well as their hydrolysis products **2'b-h** and **3'b-h**, respectively (Scheme 2). In order to characterize these complex reaction mixtures in most cases ketals were quantitatively hydrolyzed to the corresponding ketones. The products were investigated before and after hydrolysis by means of NMR spectroscopy and GC/MS measurements.

Catalytic features and regioselectivities for an addition of methanol to disubstituted alkynes catalyzed by **1** are summarized in Table 1. Generally, the reactions with alk-2-yne (Table 1; entries **c** and **d**) were found to proceed faster than with the corresponding alk-3-yne (entries **a** and **g**). In contrast to diphenylacetylene, which was unreactive under comparable reaction conditions, both additions of methanol to alkynes bearing one phenyl substituent led to the formation of the desired products (entries **f** and **h**). Furthermore, the addition to 4,4-

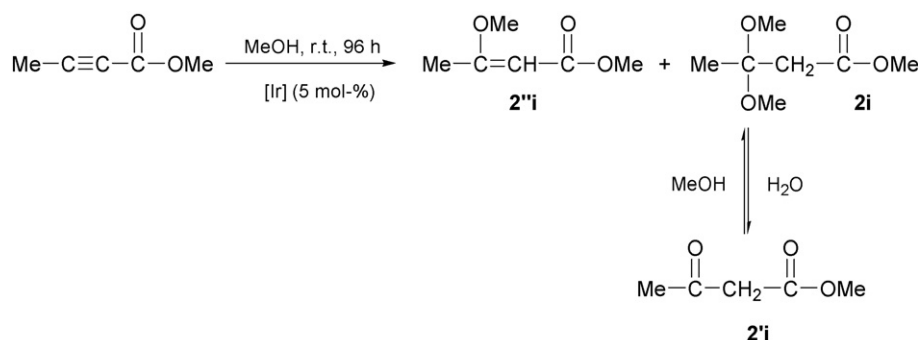


Scheme 1.

Table 1

Catalytic features and regioselectivities in an addition of methanol to disubstituted alkynes  $\text{RC}\equiv\text{CR}'$  catalyzed by  $[\text{Na}(\text{18C6})]_2[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$  (**1**)

Entry	R/R'	$n_{\text{alk.}}:n_{\text{cat.}}$	$T$ (°C)	$t$ (h)	Degree of conversion (%) <sup>a</sup>	2/2':3/3' (%) <sup>a</sup>
<b>a</b>	Et/Et	50:1	60	72	100	
	Et/Et	10:1	60	19	100	
<b>b</b>	Me/Et	20:1	45	18	100	83:17
<b>c</b>	Me/ <i>n</i> Pr	50:1	60	48	100	80:20
<b>d</b>	Me/ <i>n</i> Bu	10:1	45	24	100	85:15
<b>e</b>	Me/ <i>t</i> Bu	10:1	60	96	100 <sup>b</sup>	0:100
<b>f</b>	Me/Ph	10:1	60	48	100	58:42
<b>g</b>	Et/ <i>n</i> Pr	20:1	60	48	100	53:47
<b>h</b>	Et/Ph	10:1	60	48	95	65:35
<b>I</b>	Me/ $\text{CO}_2\text{Me}$	20:1	25	96	100	0:100
<b>j</b>	$\text{CO}_2\text{Me}/\text{CO}_2\text{Me}$	20:1	45	36	100	– <sup>c</sup>

<sup>a</sup> Determined by NMR spectroscopy, 0–10% of by-products.<sup>b</sup> 10–15% of by-products.<sup>c</sup> See Scheme 4.

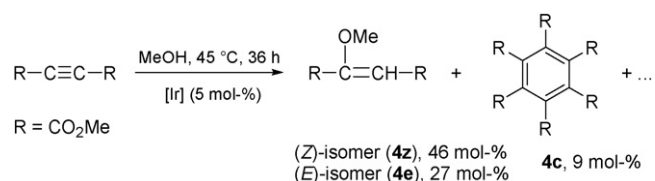
Scheme 3.

dimethylpent-2-yne was found to proceed only at 60 °C (entry **e**). Only in this case the formation of a stable vinyl ether, 2-methoxy-4,4-dimethylpent-2-ene, was observed NMR spectroscopically in the course of the reaction, presumably due to the stabilizing effect of a *t*Bu group. The regioselectivity of an iridium-catalyzed addition of methanol to internal alkynes is governed by steric and electronic factors. Thus, methanol is preferably added at a carbon atom with a longer alkyl chain or with an aromatic ring and the regioselectivities up to 85% for alk-2-yne were observed. Only in the case of hept-3-yne the addition took place at both carbon atoms of a triple bond with the same regioselectivity ca. 50% (Table 1; entry **g**). For 4,4-dimethylpent-2-yne only one addition pattern was observed, with two methoxy groups added to the methyl-substituted carbon atom. Obviously, it must be due to steric hindrance at a carbon atom with a bulky *t*Bu substituent that prevents from the addition of methoxy groups.

An addition of methanol to disubstituted functionalized alkynes catalyzed by **1** has been investigated on methyl but-2-ynoate and dimethyl but-2-yndioate. Using 5 mol% iridium catalyst, methyl but-2-ynoate was regioselectively converted into methyl 3,3-dimethoxybutanoate (**2i**) and methyl 3-oxobutanoate (**2'i**) via a vinyl intermediate, methyl 3-methoxybut-2-enoate (**2''i**) that was observed in the reaction mixture even after 4 days (Scheme 3). This reaction could be carried out only at room temperature because long heating at 45 or 60 °C resulted in the

formation of several unidentified products observed in the <sup>13</sup>C NMR spectrum.

The analogous reaction with dimethyl but-2-yndioate,  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  at 45 °C yielded 27 mol% of (*E*)-(**4e**) and 46 mol% of (*Z*)-dimethyl 2-methoxybut-2-enedioate (**4z**) as indicated by NMR spectroscopy (Scheme 4). Furthermore, in this case the addition of methanol to a triple bond yielding the vinyl ethers **4e** and **4z** was found to compete with cyclotrimerization of the alkyne to hexamethyl benzene-1,2,3,4,5,6-hexacarboxylate (**4c**, 9 mol%). The fourth product (18 mol%) could not be identified but a comparison of NMR data with those for dimethyl maleate and dimethyl fumarate excluded these two compounds as potential products. Such cyclooligomerization of alkynes is probably the most common reaction of alkynes in the presence of transition metals complexes [13]. Several iridium complexes, e.g. *trans*- $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  [14] and *trans*- $[\text{IrR}(\text{CO})(\text{PPh}_3)_2]$  (R = Me,



Scheme 4.

Table 2  
Catalytic activity of iridium compounds in the addition of methanol to hex-3-yne yielding 3,3-dimethoxyhexane (**2a**) and hexan-3-one (**2'a**) ( $T=45^\circ\text{C}$ ,  $n_{\text{hex-3-yne}}:n_{\text{cat.}} = 11:1$ )

Entry	Oxidation state of Ir	Compound	$t$ (days)	Degree of conversion (%)
1	IV	$[\text{Na}(\text{18C6})_2[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$ ( <b>1</b> )	2	98 <sup>a</sup>
2	IV	$\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$ ( <b>5</b> )	4	95 <sup>b,c</sup>
3	IV	$\text{H}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$ ( <b>6</b> )	3.5	83 <sup>b,c</sup>
4	III	$\text{Na}_3[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$ ( <b>7</b> )	5–6	93 <sup>b</sup>
5	III	$[(\text{IrCl}_2\text{Cp}^*)_2]^{\text{d}}$ ( <b>8</b> )	4	10
6	I	$[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ ( <b>9</b> )	4	5 <sup>e</sup>

<sup>a</sup> <5% of by-products.

<sup>b</sup> 5–15% of by-products.

<sup>c</sup> Reduction to Ir(III) after a few hours.

<sup>d</sup>  $n_{\text{hex-3-yne}}:n_{\text{cat.}} = 20:1$ .

<sup>e</sup> Heterogeneous reaction.

$\text{CH}_2\text{CMe}_3$ ) [15], have also been reported to cyclotrimerize activated alkynes such as  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ .

Besides complex **1**, the activity of other iridium compounds in the addition of methanol to hex-3-yne has been investigated and the results are presented in Table 2. Thus, it was found that ionic hexachloroiridates generally exhibited a catalytic activity in this direction. Our investigations show that this activity decreases in the order:  $[\text{Na}(\text{18C6})_2[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$  (**1**) >  $\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**5**)  $\approx$   $\text{H}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**6**) >  $\text{Na}_3[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$  (**7**). On the other hand, iridium(I) Vaska complex  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  (**9**) and iridium(III) pentamethylcyclopentadienyl dimer  $[(\text{IrCl}_2\text{Cp}^*)_2]$  (**8**) were almost inactive (degree of conversion <10%). The higher activity of the crown ether adduct of sodium hexachloroiridate(IV) (**1**) in comparison with **5** may be rationalized in terms of weaker cation-anion interactions. In the cases of  $\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**5**) and  $\text{H}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**6**) after a few hours a change of color from brown to orange-brown or yellow-greenish occurred, indicating presumably a partial reduction of  $[\text{IrCl}_6]^{2-}$  to  $[\text{IrCl}_6]^{3-}$  that is commonly observed in alcoholic media [16]. However, sodium hexachloroiridate(III) (**7**) was also found to catalyze the addition of methanol to hex-3-yne with a degree of conversion up to 93%.

Catalytic features such as reaction times or the  $n_{\text{alkyne}}:n_{\text{catalyst}}$  ratio in reactions catalyzed by **1** are comparable with those reported in literature for other catalytic systems based on Hg(II) [2], Pt(II)/Ag(I) [4c,d] or Pt(II) [4e]. However, the catalytic activity of **1** is remarkably lower than that of the cationic Au(I) complexes of the type  $[\text{Au}(\text{PR}_3)]^+$ , which seem to be the best systems for an addition of alcohols to alkynes ( $n_{\text{alkyne}}:n_{\text{catalyst}} = 10^5:1$ ) [6a].

Our results show for the first time that, similarly to tetra- and hexachloroplatinate complexes, hexachloroiridate analogues, especially the 18-crown-6 ether adduct  $[\text{Na}(\text{18C6})_2[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$  (**1**) are capable of catalyzing an addition of methanol to diverse disubstituted alkynes leading to the formation of ketals.

### 3. Experimental

All reactions and manipulations were carried out under argon using standard Schlenk techniques. Deuterated water-

free solvents ( $\text{CD}_3\text{OD}$ ,  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ ) were used as received. Methanol was dried over Mg and distilled from  $\text{NaBH}_4/\text{Na}_2[\text{Fe}(\text{pc})]\cdot 5.5\text{THF}$  ( $\text{H}_2\text{pc} = \text{phthalocyanine}$ ).  $\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**5**),  $\text{H}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**6**),  $\text{Na}_3[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$  (**7**),  $[(\text{IrCl}_2\text{Cp}^*)_2]$  (**8**),  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$  (**9**) and all alkynes were commercially available and used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian Gemini 200, VXR 400 and Unity 500 spectrometers. Chemical shifts are relative to  $\text{CHCl}_3$  ( $\delta$  7.24),  $\text{CHDCl}_2$  ( $\delta$  5.32),  $\text{CHD}_2\text{OD}$  ( $\delta$  3.30) and  $\text{CDCl}_3$  ( $\delta$  77.0),  $\text{CD}_2\text{Cl}_2$  ( $\delta$  53.8),  $\text{CD}_3\text{OD}$  ( $\delta$  49.0) as internal references. Assignment of NMR signals, if necessary, was revealed with a help of the  $^{13}\text{C}$  APT and NMR correlation experiments. Microanalyses (C, H) were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (Elementar Analysensysteme) elemental analyzers. IR spectra were recorded on a Mattson Galaxy 5000 FT-IR spectrometer using CsBr pellets. 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). Thermogravimetric investigations were performed using a Netzsch STA 409C thermal analysis system.

#### 3.1. Synthesis of $[\text{Na}(\text{18C6})_2[\text{IrCl}_6]\cdot x\text{H}_2\text{O}$ (**1**)

In a typical synthesis of **1**, a violet suspension of  $\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$  (**5**) (0.31 g, 0.55 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was combined at room temperature with a solution of 18-crown-6 (0.67 g, 2.53 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.5 ml). A change of color from violet to brown was observed. After a few hours the solvent volume was reduced in vacuo to about 3 ml and diethyl ether was added (3:1) to accomplish precipitation. The resulting orange-red to orange-brown precipitate was then filtered off, washed with diethyl ether (20 ml) and dried in vacuo at  $90^\circ\text{C}$ .

$x = 0.5\text{--}3.0$  (calculated by means of TGA). Yield ( $x = 3$ ): 0.48 g (85%).

Anal. Found: C, 27.33; H, 4.96; Cl, 20.46.  $\text{IrCl}_6\text{Na}_2\text{O}_{15}\text{C}_{24}\text{H}_{54}$  (1033.60). Calc.: C, 27.89; H, 5.27; Cl, 20.58. mp:  $191\text{--}194^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz):  $\delta$  3.58 (s).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100.6 MHz):  $\delta$  71.0. IR:  $\nu_{\text{Ir-Cl}}$  310(m),  $\nu_{\text{C-O}}$  1102(s)  $\text{cm}^{-1}$ .

### 3.2. Catalytic reactions

In a Schlenk test-tube  $[\text{Na}(\text{18C6})]_2[\text{IrCl}_6] \cdot x\text{H}_2\text{O}$  (**1**) (0.020–0.031 mmol) was dissolved in a  $\text{CD}_2\text{Cl}_2/\text{CH}_3\text{OH}$  or  $\text{CDCl}_3/\text{CH}_3\text{OH}$  solution (0.8–1 ml, less than 40% vol. of  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$ ). An alkyne ( $n_{\text{alkyne}}:n_{\text{catalyst}} = 10:1\text{--}50:1$ ) 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 45 or 60 °C. In appropriate time intervals  $^1\text{H}$  and  $^{13}\text{C}$  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  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra with those of authentic samples or available in literature, in integrated spectral database system for organic compounds (SDBD) [17] as well as by means of GC/MS measurements. Detailed spectroscopic characterization of all organic products has been deposited as supplementary material.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.10.027.

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