

## Research paper

# Selective reduction of alkynes to alkenes with hydrogen or formic acid catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>]<sup>☆</sup>

György Hankó<sup>a</sup>, Richárd Márton<sup>a</sup>, Antal Udvardy<sup>a</sup>, Mihály Purgel<sup>a</sup>, Ágnes Kathó<sup>a</sup>,  
Ferenc Joó<sup>a,b</sup>, Gábor Papp<sup>a,\*</sup>

<sup>a</sup> Department of Physical Chemistry, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary

<sup>b</sup> MTA-DE Redox and Homogeneous Catalytic Reaction Mechanisms Research Group, P.O.Box 400, H-4002 Debrecen, Hungary



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## ABSTRACT

In this work we have found, that the water-soluble *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>] (*mtp*ppms = monosulfonated triphenylphosphine Na-salt) was an excellent catalyst for reduction of terminal alkynes by hydrogen transfer from aqueous HCOOH/HCOONa mixtures. The conversions strongly depended on the pH of the reaction mixtures, and the highest rate of phenylacetylene transfer hydrogenation was observed at pH 3. The same dihydrido-Ir(III) complex actively catalyzed also the hydrogenation of terminal alkynes under mild conditions (T = 50 °C; P (H<sub>2</sub>) = 2–10 bar). Importantly, both the hydrogenation and hydrogen transfer reductions afforded exclusively the corresponding alkenes as products. Phenylacetylene and its substituted derivatives reacted smoothly, while benzylic and aliphatic alkynes were less reactive or did not react at all. It was also found, that an excess of the *mtp*ppms ligand inhibited the reaction. This was rationalized by formation of *cis*-[IrH<sub>2</sub>(*mtp*ppms)<sub>4</sub>]<sup>+</sup> which was also confirmed with multinuclear NMR spectroscopy. On the basis of the experimental results, a joint mechanism was suggested for both the hydrogenation and transfer hydrogenation pathways. The mechanism of hydrogenation and transfer hydrogenation of phenylacetylene was also studied by DFT calculations, which revealed several possibilities for protonation of a vinyl intermediate as the crucial step in formation of the styrene product.

## 1. Introduction

The selective hydrogenation of unsaturated organic compounds is a highly significant research area from a practical point of view, because the resulting partially or fully hydrogenated derivatives are important materials of the fine chemical industry. From the pharmaceutical or perfume industries to the manufacturing of pesticides, it is increasingly important to develop more efficient and cost-effective processes. Thus, the heterogeneous or homogeneous catalytic selective hydrogenation of polyunsaturated compounds is a key aspect of catalysis research.

Heterogeneous catalysts suitable for the semi-hydrogenation of alkynes are widely known in the literature [1–3] and numerous transition metal complexes proved to be highly active in these reactions in homogeneous phase as well [4–8]. Homogeneous catalysis is accompanied

by the problem of separating the catalysts from the products, and catalyst recycling is also difficult [9]. One potential method for capitalizing on the efficiency and selectivity characteristic of homogeneous catalysts is performing aqueous-organic biphasic catalysis. In this case, the water-soluble catalyst (obtained –for example– by incorporating water-soluble ligands, such as e.g. sulfonated triphenylphosphines into the metal complex catalysts) is easily separable from the organic products (or reagents) and is recyclable [6,10].

A safer alternative for hydrogenation is the method of hydrogen transfer from suitable hydrogen donor substances. In these cases, the hydrogen source is not gaseous hydrogen (often under high pressure), but amine-borane [11], alcohol/base (EtOH [12,13], MeOH [14], 2-PrOH [15]), hypophosphorous acid [16], or in several cases HCOOH/HCOONa [17–21], to name a few.

**Abbreviations:** *mtp*ppms, monosulfonated triphenylphosphine Na-salt (3-diphenylphosphinobenzenesulfonic acid Na-salt); *mtp*pts, trisulfonated triphenylphosphine trisodium salt (trisodium 3,3',3''-phosphinetriylbenzenesulfonate); TOF, turnover frequency = (mol reacted substrate) × (mol catalyst × time)<sup>−1</sup> = TON × time<sup>−1</sup>; TON, turnover number = (mol reacted substrate) × (mol catalyst)<sup>−1</sup>; PMe<sub>3</sub>, trimethylphosphine; PPh<sub>3</sub>, triphenylphosphine.

<sup>☆</sup> Dedicated to **Professor Maurizio Peruzzini** on the occasion of his 65th birthday in recognition of his numerous achievements in coordination chemistry and homogeneous catalysis.

\* Corresponding author.

E-mail address: [papp.gabor@science.unideb.hu](mailto:papp.gabor@science.unideb.hu) (G. Papp).

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$[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$  has long been known as a hydrogenation catalyst [22]. Seminal papers on water-soluble Ir(I)-phosphine complexes were published by Atwood et al, whose work mostly dealt with carbonyl complexes including *cis,mer*- $[\text{IrH}_2(\text{CO})\text{L}_3]^+$  ( $\text{L} = \text{mtppps}$ , *mtppts*), too [23–28]. Merola and co-workers made extensive studies on the synthesis and aqueous organometallic chemistry of *mer*- $[\text{IrH}_2\text{X}(\text{PMe}_3)_3]$  complexes ( $\text{PMe}_3 = \text{trimethylphosphine}$ ,  $\text{X} = \text{various halides or other anions}$ ) [29,30]. However, it was only in 2016, that our research group first published the synthesis of the closest water-soluble analog of  $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$ , *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$ , and its first application in selective  $\text{HCOOH}$  decomposition [31]. It was established that this catalyst performed the fastest hydrogen evolution from aqueous formic acid/formate solutions (max. TOF = 298 000  $\text{h}^{-1}$ ; max. TON = 67 650). Furthermore, it was successfully demonstrated that the catalyst was recyclable without significant loss of activity –  $\text{HCOOH}$  decomposition was carried out with the same catalyst in five consecutive cycles.

The same catalytic system was used in the high-resolution analytical assay of glycans, in which the reaction is technically a homogeneous phase reductive amination [32].  $\text{HCOOH}$  acted as a hydrogen source in our method, substituting the highly toxic, but still widely used cyanoborohydride. The *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  catalyst was investigated in the *para*-hydrogenation of various water-soluble alkyne derivatives, too, where the semi-hydrogenated alkene products maintained the enhanced magnetically labeled signals. Accordingly, these catalytic systems have the potential to be applied in medical diagnostics [33].

In this publication, we describe the application of *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  dihydride in the selective hydrogenation of various alkyne derivatives (Scheme 1). Both gaseous hydrogen and aqueous  $\text{HCOOH}/\text{HCOONa}$  mixtures were used as hydrogen sources in aqueous-organic biphasic reactions.

## 2. Experimental section

### 2.1. Materials and methods

*cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  [31] and *mtppps* [34] were synthesized as described earlier and their purities were checked by NMR spectroscopy. Phenylacetylene and other alkynes were purchased from Sigma-Aldrich and used as received.  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was obtained from Pressure Chemical Co. and Alfa Aesar.  $\text{HCOOH}$ ,  $\text{HCOONa}$ , and other inorganic salts were supplied by Sigma-Aldrich and VWR. Argon, nitrogen and hydrogen (99.99% purity) were provided by Linde. Deuterated solvents (99.9%) were purchased from Cambridge Isotope Laboratories Inc. and Sigma-Aldrich. NMR spectra were recorded on BRUKER AVANCE DRX 360 and BRUKER AVANCE I 400 MHz spectrometers and evaluated using the Bruker TopSpin program.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were referenced to tetramethylsilane (TMS), 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), 85%  $\text{H}_3\text{PO}_4$  and residual solvent peaks, respectively. Gas chromatographic measurements were performed with the use of an Agilent Technologies 7890 A instrument (Optima®-1, 0.25  $\mu\text{m}$ , 30 m  $\times$  0.32 mm, FID 300  $^\circ\text{C}$ , carrier gas: Nitrogen 1.9  $\text{mL min}^{-1}$ ).

### 2.2. General procedure for the hydrogenation and transfer hydrogenation of alkynes

All manipulations were performed under oxygen-free conditions using standard Schlenk-techniques. The solid catalyst, excess of phosphine ligand (if required), and naphthalene (internal standard) were

placed into a home-made medium pressure glass reactor fitted with a silicon rubber septum (total volume  $80 \pm 2$  mL) which –after several vacuum/argon cycles– was finally filled with atmospheric Ar. The solvents were added through the septum with a syringe/hypodermic needle and the solids were dissolved with magnetic stirring. After the addition of the substrate solution, the reactor was filled with  $\text{H}_2$ -gas up to the desired pressure, placed into a thermostated bath and the reaction mixture was stirred vigorously. At the desired reaction time, the reactor was cooled down in crushed ice, vented slowly and opened to air. The liquid phases were separated, a sample of the organic phase was dried by passing through a plug of anhydrous  $\text{MgSO}_4$ , and was analyzed by gas chromatography.

For transfer hydrogenation of alkynes, the  $\text{H}_2$  atmosphere in the reactor was replaced with Ar, and aqueous solutions of  $\text{HCOOH}$  and  $\text{HCOONa}$  were used instead of water as the aqueous phase.

### 2.3. Computational details

DFT calculations [35] were carried out using Gaussian09 software package [36]. Geometry optimizations were performed with M06 functional [37] Def2TZVP ECP/basis set was employed on iridium [38], together with the TZVP basis set for non-metal atoms [39,40]. Frequency calculations were done at the level of the theory of geometry optimization. Relative free energies ( $\Delta G$ ) are reported at 298.15 K and atmospheric pressure. The solvent (water) effect was accounted for with the use of the Polarized Continuum Model (IEF-PCM) [41]. Stationary points on the Potential Energy Surface (PES) are reactants (R), intermediates (I), transition states (TS), and products (P) as first-order saddle points of PES. All stationary points were confirmed by frequency analysis where minima had all positive frequencies while TSs had one imaginary frequency related to the actual movement of the reaction coordinate. For the calculations, the sulfonated phosphine ligands in *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  and its derivatives were replaced by  $\text{PPh}_3$ .

## 3. Results and discussion

### 3.1. Hydrogenation of alkynes catalyzed by *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$

The catalytic properties of *cis,mer*- $[\text{IrH}_2\text{Cl}(\text{mtppps})_3]$  was studied in

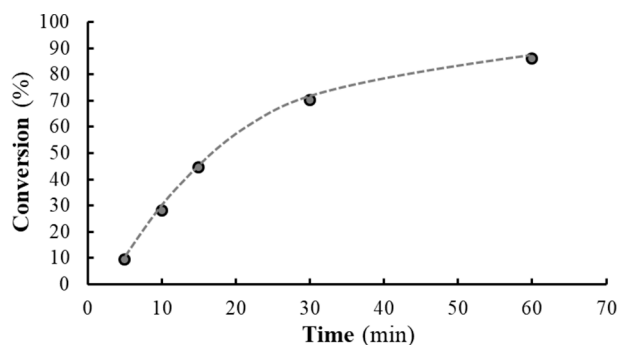
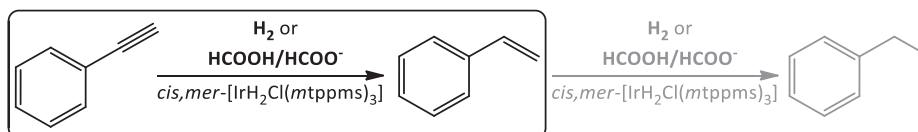


Fig. 1. Hydrogenation of phenylacetylene in aqueous-organic biphasic system. Conditions:  $n_{\text{phenylacetylene}} = 5 \times 10^{-4}$  mol;  $V_{\text{H}_2\text{O}} = 5.0$  mL;  $V_{\text{toluene}} = 3.0$  mL;  $T = 50$   $^\circ\text{C}$ ;  $P(\text{H}_2) = 10$  bar; 1 mol% catalyst.



Scheme 1. Hydrogenation of phenylacetylene.

detail in hydrogenation of phenylacetylene in aqueous-organic biphasic reactions. Time course of the reaction is shown by Fig. 1.

As shown by Fig. 1, *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] efficiently catalyzed the hydrogenation of phenylacetylene even under mild reaction conditions (50 °C, 10 bar H<sub>2</sub>, 1 mol% catalyst). The turnover frequency, TOF, calculated from the initial linear part of the conversion vs. reaction time graph, reached 180 h<sup>-1</sup> (TOF = (mol reacted substrate) × (mol catalyst × time)<sup>-1</sup>). This TOF compares favorably to those in the literature [4,5,8] given the biphasic nature of the reaction mixture and the low solubility (456 mg/L at 25 °C [42]) of phenylacetylene in water.

The rate of hydrogenation increased with rising temperature, and under the conditions of Fig. 1 but at 80 °C temperature, the reaction time needed for 100% conversion of phenylacetylene to styrene was less than 10 min (which implies TOF = 600 h<sup>-1</sup> as a lower limit). An increase of hydrogen pressure from 2 to 10 bar led to an approximately threefold increase in the reaction rate (Table S1).

An important feature of the reaction is its selectivity to the alkene product. In no experiments in this study, was formation of products other than styrene detected in hydrogenation of phenylacetylene with *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] as the catalyst. For example, even when a reaction was performed at 80 °C for 2 h (other conditions as at Fig. 1), only semi-hydrogenation to styrene was observed, despite a 100% conversion of phenylacetylene to styrene within the first 10 min. Under our conditions, the products of alkyne hydration/hydrogenation (i.e. ketones and alcohols) – as described by Luo et al. [43] and Xiao et al. [44] – were not detected.

The study of phenylacetylene conversion as a function of the substrate to catalyst concentration ratio ([S]/[C]) revealed an important feature of the reaction. As shown in Fig. 2, the conversion decreased only slightly in the [S]/[C] = 100–200 interval, however, this was followed by a sharp drop, so much that at [S]/[C] = 1000, only a 3% conversion was determined. In the [S]/[C] = 100–1000 range, the TOF values varied according to a maximum curve. It is noteworthy that even at the highest alkyne concentration the specific reaction rate (expressed as TOF) still was about 20% of its highest value. Furthermore, the selectivity to styrene was retained at all [S]/[C] conditions.

The likely reason for this phenomenon may be in substrate inhibition occurring at higher concentrations. Since the minimum substrate concentration is 100 times higher than that of the catalyst, formation of a presumed unreactive *bis*(alkyne)Ir(III) species would not decrease significantly the total available substrate concentration but could decrease the concentration of the catalytically active Ir-species substantially (see also the suggested mechanism in Section 3.3).

In addition to phenylacetylene, hydrogenation of 4-ethynylbromobenzene and 3-phenyl-1-propyne (benzylacetylene) were also

attempted with *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] as the catalyst. Importantly, these two substrates also afforded the corresponding alkenes as exclusive products. However, their reaction rates were largely different: under the conditions of Fig. 1, but at 80 °C, the required reaction time for 100% conversion was 90 min with 4-ethynylbromobenzene and 240 min with benzylacetylene, compared to less than 10 min with phenylacetylene. Aliphatic alkynes (4-phenyl-1-butyne and 1-hexyne) were not hydrogenated and diphenylacetylene proved unreactive, too.

### 3.2. Transfer hydrogenation of phenylacetylene

Reductions with hydrogen transfer from suitable donor molecules instead of molecular H<sub>2</sub> have several advantages over conventional hydrogenations [45]. In addition to alcohols (most often 2-propanol), applied together with appropriate bases, formic acid, formates or their mixtures are often used as sources of hydrogen for the most diverse reactions [8,45].

We have described earlier, that *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] was an outstandingly active catalyst for the decomposition of formic acid in the presence of Na-formate [31]. The reaction rate strongly depended on the solution pH, i.e. on the [HCOOH]/[HCOONa] ratio in the reaction mixture (actually, the aqueous formic acid/formate mixture served as a pH buffer, too). In addition, *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] was also used as the catalyst in a reductive amination-based analytical method [32], in which the reduction of an imine was achieved by catalytic H-transfer from HCOOH.

Based on the above findings, we attempted transfer hydrogenation of phenylacetylene and other alkynes using *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] as the catalyst. Indeed, the reaction proceeded with reasonable rates, leading to 67% conversion with 1 mol% catalyst at 80 °C at pH 2.9 (Fig. 3). This conversion corresponds to TOF = 34 h<sup>-1</sup>, which is comparable to the TOF observed in hydrogenations of the same substrate with the same catalyst at T = 50 °C and 10 bar H<sub>2</sub> pressure.

As can be seen on Fig. 4, the rate of transfer hydrogenation of phenylacetylene as the function of the pH of the formate buffer showed a sharp maximum at pH ~ 3 when [HCOOH]/[HCOO<sup>-</sup>] is 7/3.

The data of Fig. 4 may explain the slowing down of the transfer hydrogenation after the first 0.5–1 h reaction time, as appears on Fig. 3. Since the reaction is slow in neutral or basic solutions, it may be supposed, that the actual hydride donor is HCOOH. With increasing reaction times, not only the concentration of one of the reactants (HCOOH) is decreased, but the consumption of formic acid leads to a gradual increase of the pH of the mixture, too. Consequently, these two effects result in a steady decrease of the rate of further hydrogen transfer to phenylacetylene.

The rate of the reaction showed strong dependence on the temperature (Figure S2). An Arrhenius-type plot of the TOF values as the

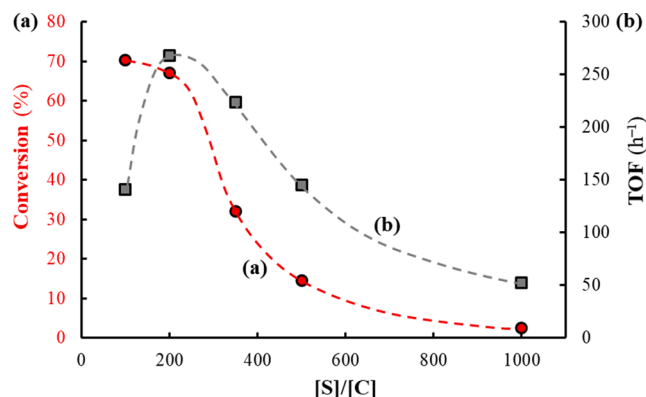


Fig. 2. Conversion of the substrate (a) and turnover frequency of the catalyst (b) in hydrogenation of phenylacetylene catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] as functions of the substrate to catalyst concentration ratio ([S]/[C]). Conditions:  $n_{\text{catalyst}} = 5 \times 10^{-6}$  mol;  $V_{\text{H}_2\text{O}} = 5.0$  mL;  $V_{\text{toluene}} = 3.0$  mL; T = 50 °C; P(H<sub>2</sub>) = 10 bar, t = 30 min.

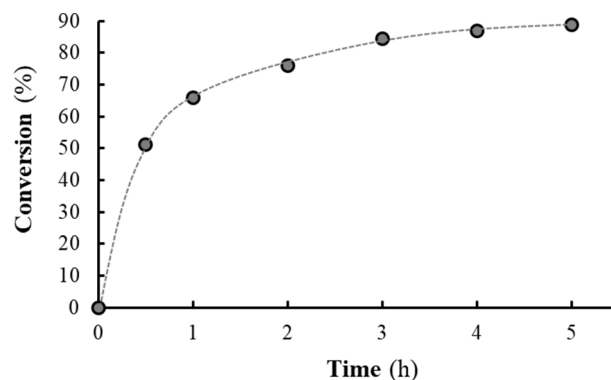
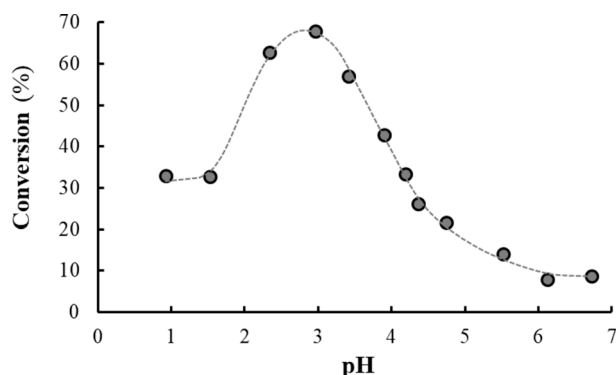


Fig. 3. Time course of the transfer hydrogenation of phenylacetylene in aqueous-organic biphasic system catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>]. Conditions:  $n_{\text{catalyst}} = 5 \times 10^{-6}$  mol;  $n_{\text{substrate}} = 5 \times 10^{-4}$  mol;  $V_{\text{H}_2\text{O}} = 6.0$  mL;  $V_{\text{toluene}} = 3.0$  mL; T = 80 °C; ( $n_{\text{HCOOH}} + n_{\text{HCOONa}}$ )<sub>0</sub> =  $4.0 \times 10^{-3}$  mol; pH = 2.9;



**Fig. 4.** Conversion of phenylacetylene as a function of pH in transfer hydrogenation from HCOOH/HCOONa catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>]. Conditions:  $n_{\text{catalyst}} = 5 \times 10^{-6}$  mol;  $n_{\text{substrate}} = 5 \times 10^{-4}$  mol;  $V_{\text{H}_2\text{O}} = 6.0$  mL;  $V_{\text{toluene}} = 3.0$  mL;  $T = 80$  °C;  $(n_{\text{HCOOH}} + n_{\text{HCOONa}})_0 = 2.0 \times 10^{-3}$  mol;  $t = 2$  h.

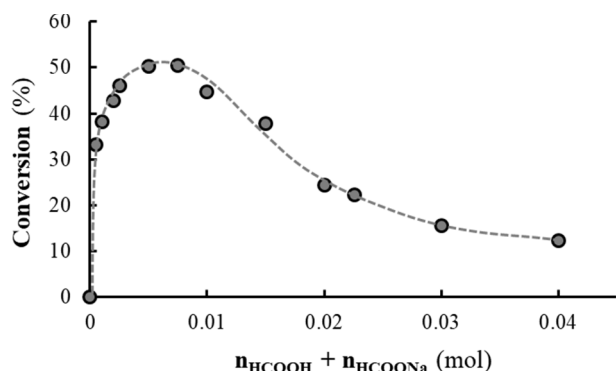
function of the inverse absolute temperature yielded a temperature coefficient of 21.3 kJ/mol (Figure S3). However, in lack of more detailed kinetic experiments and data, this number can be regarded only as a composite value representing also the temperature dependence of the partition equilibrium of phenylacetylene between the aqueous and the toluene phase.

It is important to note here, that similar to the hydrogenations with H<sub>2</sub>, transfer hydrogenation of phenylacetylene from formic acid/formate also resulted in formation of styrene with 100% selectivity.

The effect of the total amount of the H-donor (i.e. the concentration of the formate buffer) was also established. In these experiments the pH was set to a constant 3.9, and only the [H-donor]/[substrate] ratio was varied – the results are shown on Fig. 5. As expected, at the beginning the conversion increased with the increased amount of the H-donor, however, after reaching a sharp maximum at  $n_{\text{HCOOH}} + n_{\text{HCOONa}} = 7.5 \times 10^{-3}$  mol, it showed a gradual drop with further increase of the total formic acid/formate concentration. In the specific case of Fig. 5, the maximum conversion was observed at the [H-donor]:[substrate]:[catalyst] = 1500:100:1 ratio.

At the moment we do not have a clear explanation of the large drop in phenylacetylene conversion at large formic acid/formate concentrations. In more concentrated electrolyte solutions, some salting out of phenylacetylene from the aqueous phase may happen. Alternatively, the increased HCOO<sup>−</sup> concentration should facilitate the coordination of this ion to the cationic Ir(III) complexes which –presumably– act as the active species in the catalytic cycle (see below).

Concerning other alkynes it was found, that while the transfer

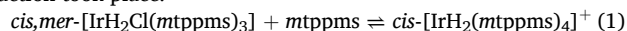


**Fig. 5.** Transfer hydrogenation of phenylacetylene from formic acid/formate mixtures catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>]: conversion of the alkyne as a function of the total amount of the H-donor ( $n_{\text{HCOOH}} + n_{\text{HCOONa}}$ ). Conditions:  $n_{\text{catalyst}} = 5 \times 10^{-6}$  mol;  $n_{\text{substrate}} = 5 \times 10^{-4}$  mol;  $V_{\text{H}_2\text{O}} = 6.0$  mL;  $V_{\text{toluene}} = 3.0$  mL; pH = 3.90;  $T = 80$  °C;  $t = 2$  h.

hydrogenation of phenylacetylene resulted in 43% conversion, and 4-ethynylanisole (37% conversion) and 4-ethynyltoluene (45% conversion) also reacted smoothly, then 4-ethynyl-bromobenzene showed only 18% conversion. In contrast, diphenylacetylene, 3-phenyl-1-propyne, 4-phenyl-1-butyne, and 1-hexyne did not react at all (conditions:  $n_{\text{catalyst}} = 5 \times 10^{-6}$  mol;  $n_{\text{substrate}} = 5 \times 10^{-4}$  mol;  $V_{\text{H}_2\text{O}} = 6.0$  mL;  $V_{\text{toluene}} = 3.0$  mL; pH = 3.90;  $n_{\text{HCOOH}} = n_{\text{HCOONa}} = 7.5 \times 10^{-3}$  mol;  $T = 80$  °C;  $t = 1$  h).

With the aim to get some insight into the reaction mechanism, we studied the effect of added phosphine ligand on the rate of phenylacetylene reduction by hydrogen transfer from formic acid/formate mixtures with *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>] as the catalyst. The results are presented in Table 1.

As can be seen from the data of Table 1, the conversion of phenylacetylene gradually decreased with increased *mtp*ppms concentration, approaching only half of the original conversion at a 5-fold ligand excess over *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>]. In addition, <sup>1</sup>H and <sup>31</sup>P NMR measurements revealed, that upon the addition of *mtp*ppms, the following reaction took place:



Note, that in this reaction a coordinated halide is replaced relatively easily by a phosphine ligand giving rise to a cationic complex. This behaviour is not without precedent in aqueous solutions, where both the halide anion and the complex cation become stabilized by strong hydration [29,30,46]. Merola and co-workers synthesized a similar compound *cis,mer*-[IrH<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>3</sub>], which, in aqueous solution, underwent replacement of chloride by PMe<sub>3</sub> in a process analogous to Equation 1 [29,30].

The <sup>1</sup>H and <sup>31</sup>P NMR parameters of *cis*-[IrH<sub>2</sub>(*mtp*ppms)<sub>4</sub>]<sup>+</sup> formed by the exchange of halide to *mtp*ppms are displayed in Fig. 6.

Since the NMR measurements were performed at 25 °C in MeOH/H<sub>2</sub>O mixed solvent, the results cannot be strictly paralleled with the catalytic results determined at 80 °C. Nevertheless, it is safe to say, that the catalytic activity of *cis*-[IrH<sub>2</sub>(*mtp*ppms)<sub>4</sub>]<sup>+</sup> is lower than that of the initial *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>] complex.

### 3.3. Suggested mechanism of hydrogenation or hydrogen transfer reduction of phenylacetylene catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>]

Based on the experimental results described in Sections 3.2 and 3.3, we suggest the following mechanism for the reduction of phenylacetylene both by hydrogenation (involving H<sub>2</sub>) and by transfer hydrogenation (involving formic acid/formate mixtures as H-donor) (Scheme 2).

According to this mechanism, in the first step of the reaction, a water molecule coordinates in place of the halide of *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>] (A), yielding *cis,mer*-[IrH<sub>2</sub>(H<sub>2</sub>O)(*mtp*ppms)<sub>3</sub>]<sup>+</sup> (B), the entry point to the catalytic cycle. Formation of this aquo species was confirmed by determination of chloride with the use of a chloride selective electrode: in a 1.00 mM aqueous solution of *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>], [Cl<sup>−</sup>] = 0.96 mM was found experimentally (for details see Supporting Information). The labile water ligand in this complex is later replaced by the substrate phenylacetylene yielding C. Hydride migration to the β-carbon

**Table 1**  
Effect of added *mtp*ppms on transfer hydrogenation of phenylacetylene catalyzed by *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>] and on formation of *cis*-[IrH<sub>2</sub>(*mtp*ppms)<sub>4</sub>]<sup>+</sup>.

[ <i>mtp</i> ppms]/[IrH <sub>2</sub> Cl( <i>mtp</i> ppms) <sub>3</sub> ]	Conversion (%)	<i>cis</i> -[IrH <sub>2</sub> ( <i>mtp</i> ppms) <sub>4</sub> ] <sup>+</sup> (%) *
0	53	0
1	33	20
3	29	33
5	30	57

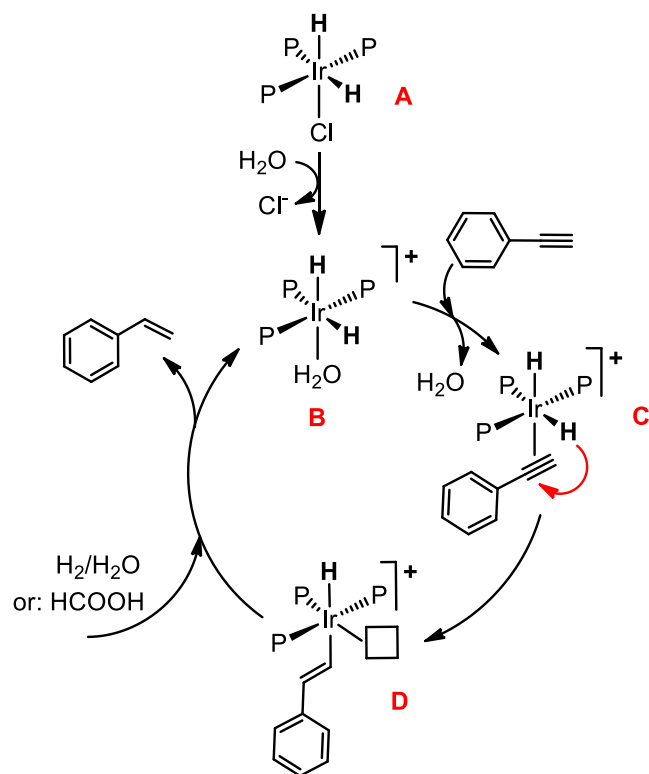
Conditions:  $n_{\text{substrate}} = 5 \times 10^{-4}$  mol;  $V_{\text{H}_2\text{O}} = 6.0$  mL;  $V_{\text{toluene}} = 3.0$  mL;  $T = 80$  °C;  $t = 2$  h;  $n_{\text{HCOOH}} = n_{\text{HCOONa}} = 7.5 \times 10^{-3}$  mol; pH = 3.90; 1 mol% catalyst.

\* Molar ratio of *cis*-[IrH<sub>2</sub>(*mtp*ppms)<sub>4</sub>]<sup>+</sup> in the *cis,mer*-[IrH<sub>2</sub>Cl(*mtp*ppms)<sub>3</sub>] + *n mtp*ppms mixtures, determined by <sup>31</sup>P NMR spectroscopy ( $T = 25$  °C, solvent: MeOH-H<sub>2</sub>O).





Fig. 6. Structure and the measured NMR parameters of  $cis$ -[IrH<sub>2</sub>(mtppps)<sub>4</sub>]<sup>+</sup>.



**Scheme 2.** Suggested mechanism of phenylacetylene hydrogenation and transfer hydrogenation from formic acid/formate mixtures, catalyzed by  $cis,mer$ -[IrH<sub>2</sub>Cl(mtppps)<sub>3</sub>].

of the coordinated phenylacetylene results in a vinyl species (**D**) with a vacant coordination site on Ir. Release of styrene requires protonation on  $\alpha$ -carbon and there are several possibilities for this step:

a) The vacant site in **D** is filled by a H<sub>2</sub> molecule. Protonation of the vinyl intermediate happens from the coordinated dihydrogen and leads to release of styrene (replaced by H<sub>2</sub>O) and yields directly the catalytically active  $cis,mer$ -[IrH<sub>2</sub>(H<sub>2</sub>O)(mtppps)<sub>3</sub>]<sup>+</sup> species (**B**).

b) The vacant site in **D** is filled by a water molecule. The coordinated H<sub>2</sub>O protonates the  $\alpha$ -carbon of the neighbouring vinyl ligand leading to the release of styrene and formation of  $mer$ -[IrH(OH)(H<sub>2</sub>O)(P)<sub>3</sub>]<sup>+</sup> complex. Further reaction of this complex with H<sub>2</sub> leads to regeneration of **B**.

c) The vacant site in **D** is occupied by a formic acid molecule with monodentate coordination through its carbonyl oxygen. The coordinated formic acid protonates the  $\alpha$ -carbon of the neighbouring vinyl moiety resulting in the release of styrene and formation of [IrH(HCOO)(P)<sub>3</sub>]<sup>+</sup>. Internal redox reaction of this complex with CO<sub>2</sub> loss regenerates  $cis,mer$ -[IrH<sub>2</sub>(H<sub>2</sub>O)(mtppps)<sub>3</sub>]<sup>+</sup> (**B**).

d) The vinyl intermediate **D** is protonated by H<sup>+</sup> from the bulk of the aqueous solution. This step is more probable in acidic solutions but becomes less favoured under basic conditions.

This mechanism is in agreement with the inhibition by excess

mtppps, which –via formation of  $cis$ -[IrH<sub>2</sub>(mtppps)<sub>4</sub>]<sup>+</sup>– removes (part of) the catalytically important  $cis,mer$ -[IrH<sub>2</sub>(H<sub>2</sub>O)(mtppps)<sub>3</sub>]<sup>+</sup> from the catalytic cycle.

Another important question should be considered. Since  $cis,mer$ -[IrH<sub>2</sub>Cl(mtppps)<sub>3</sub>] is an extremely good catalyst of formic acid decomposition to H<sub>2</sub> + CO<sub>2</sub>, there is a chance for the reduction of phenylacetylene to proceed simply by hydrogenation using the H<sub>2</sub> supplied by prior formic acid decomposition. To check this possibility, phenylacetylene was injected into the reaction mixture of a fast running formate decomposition reaction which was followed by measuring the volume of the evolved gas in a thermostated gas burette. Following the addition of phenylacetylene, gas evolution slowed down immediately and completely ceased in a few minutes. Upon further stirring no change of the gas volume (neither gas evolution, nor uptake) was observed. However, after 2 h reaction time, 40% conversion of phenylacetylene to styrene was determined. This shows, that in the presence of HCOOH/HCOONa mixture, only transfer hydrogenation is operative. However, transfer hydrogenation of phenylacetylene –although comparable in rate– is slower than its hydrogenation with H<sub>2</sub>. In agreement with the results from the gas burette measurements, we did not observe development of pressure in the reactors during transfer hydrogenation reactions. These observations support the existence of two different pathways for hydrogenation and hydrogen transfer.

### 3.4. DFT calculations on phenylacetylene hydrogenation and transfer hydrogenation

We performed DFT calculations to find out which of the proposed mechanisms can be reasonable and comparable to the experimental results. We found that the coordinated phenylacetylene in the axial position is favorable (**I1**; –21.9 kJ mol<sup>–1</sup>) referred to  $cis,mer$ -[IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and outer-sphere phenylacetylene system (**R**). From this, the energy barrier of the hydride transfer's elementary step is 56.1 kJ mol<sup>–1</sup> (**TS1**; 34.9 kJ mol<sup>–1</sup>) resulting in the  $\sigma$ -styryl intermediate (**I2**; –17.0 kJ mol<sup>–1</sup>). To the vacant equatorial side, the coordination of the hydrogen molecule was the most preferred (**I3a**; –25.6 kJ mol<sup>–1</sup>) while the coordination of a water molecule was slightly favored (**I3b**; –8.9 kJ mol<sup>–1</sup>) compared to the coordination of formic acid (**I3c**; –6.3 kJ mol<sup>–1</sup>). The proton transfer was a two-step process from **I3a**: in the first step, an H–H cleavage occurred (**TS2a**; –25.3 kJ mol<sup>–1</sup>) resulting in a species in which one of the hydrogen atoms stayed in the equatorial position while the other one went to the axial position forming a hydrogen molecule in axial position (**I4a**; –66.3 kJ mol<sup>–1</sup>). From this, an interesting transition state was found (**TS3a**; –27.8 kJ mol<sup>–1</sup>) in which both hydrogen atoms had a rearrangement and therefore was similar to tetrahydride species in which one of the hydrides was replaced by the carbon atom of  $\sigma$ -styryl. The hydrogen from the axial position went back to the equatorial position while from the equatorial side the hydrogen transferred to the  $\sigma$ -styryl resulting in the final product having a dissociated styrene and the  $cis,mer$ -[IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] catalyst (**P**; –152.9 kJ mol<sup>–1</sup>). The coordinated water molecule had less preferred steric condition than hydrogen, therefore, a significantly higher energy barrier occurred (**TS2b**; 36.5 kJ mol<sup>–1</sup>). We found, however, that the  $\kappa^1$ -O state

of the coordinated formic acid had an excellent orientation which resulted in a very low energy barrier of the one-step proton transfer (**TS2c**;  $-4.4$  kJ mol $^{-1}$ ). Both proton transfers resulted in very favored intermediates (**I4b**;  $-83.8$  kJ mol $^{-1}$  and **I4c**;  $-119.0$  kJ mol $^{-1}$ ) which needed other steps to get back the *cis,mer*-[IrH $_2$ (PPh $_3$ ) $_3$ ] catalyst, see Fig. S6–S8 (Fig. 7).

### 3.5. The relative contributions of intermediates I3a–I3c to styrene release via proton transfer

As can be seen from Section 3.4, a crucial step of the mechanism is the way of protonation of the vinyl intermediate whether it is *mer*-[IrH(H $_2$ )(C $_6$ H $_5$ C $_2$ H $_2$ )(P $_3$ )] $^+$  (**I3a**) or *mer*-[IrH(H $_2$ O)(C $_6$ H $_5$ C $_2$ H $_2$ )(P $_3$ )] $^+$  (**I3b**) in hydrogenation or *mer*-[IrH(HCOOH)(C $_6$ H $_5$ C $_2$ H $_2$ )(P $_3$ )] (**I3c**) in hydrogen transfer. In neutral and basic solutions, proton concentration in the bulk aqueous reaction mixture is probably too low to favour direct protonation, although Paterniti and Atwood observed instantaneous protonation of the methyl ligand in *trans*-[Ir(CO)(Me)L $_2$ ] (L = mtpms-Na or mtpms-K) upon dissolution in water [24]. Conversely, while direct involvement of undissociated HCOOH agrees with the rate increase from pH 7 to pH 3, it seems incompatible with the decrease of the reaction rate below pH 3. The solubility of H $_2$  in water is 0.81 mM (20 °C), while the catalyst concentration in our case is 1 mM. In contrast, in such aqueous solutions, water is in a very large excess over the catalyst, and fast conversion of the starting chloro-complex (**A**) to *cis,mer*-[IrH $_2$ (H $_2$ O)(mtpms) $_3$ ] $^+$  (**B**) was demonstrated by determination of the concentration of free chloride. Merola et al have observed the same replacement of chloride by H $_2$ O in aqueous solutions of *cis,mer*-[IrH $_2$ Cl(PMe) $_3$ ] yielding *cis,mer*-[IrH $_2$ (H $_2$ O)(PMe) $_3$ ] $^+$ . They have suggested, that the mechanism of H/D exchange in *cis,mer*-[IrH $_2$ (H $_2$ O)(PMe) $_3$ ] $^+$  dissolved in D $_2$ O proceeded via protonation of a hydride ligand in the complex by the neighbouring D $_2$ O (yielded by a H $_2$ O/D $_2$ O exchange) followed by deprotonation of the resulting ( $\eta^2$ -HD)Ir species [29]. Similar H/D exchange was observed by Atwood et al. in D $_2$ O solutions of [IrClH $_2$ (CO)

(mtppts) $_2$ ] and [IrH $_2$ (CO)(mtppts) $_3$ ] $^+$ , however, no mechanism was suggested for the reactions [26]. In our case, *cis,mer*-[IrH $_2$ (H $_2$ O)(mtpms) $_3$ ] $^+$ , too, underwent H/D exchange, shown by the loss of couplings in the otherwise well-resolved  $^1$ H NMR (hydride region), as well as by the increase of the water signal intensity (see Supporting Information). This leads us to believe, that the vinyl intermediate in phenylacetylene hydrogenation may be efficiently protonated by a H $_2$ O ligand in *cis*-position.

Our DFT calculations showed that protonation by a coordinated dihydrogen of the vinyl-ligand in **D** is much preferred to protonation by coordinated H $_2$ O. However, there is precedent in the literature (other than the mentioned H/D exchange) where such an interaction was considered [47]. We have also found that coordinated water could be involved in such a protonation process in hydrogenation of cinnamaldehyde catalyzed by [{RuCl $_2$ (mtpms) $_2$ ] $_2$ ] [48]. It should also be mentioned, that taking into account the large excess of water molecule (55.5 M) relative to the concentration of hydrogen and formic acid, the energy of **I3b**, **TS2b** and **I4b** can be corrected by  $-18.0$  kJ/mol. This value is calculated by the  $-RT\ln(c_{\text{bulk}}/c_{\text{ideal gas}})$  equation, where R is 8.314 J/molK, T = 298 K,  $c_{\text{bulk}}$  = 55.5 M and  $c_{\text{ideal gas}}$  is 1/24.5 M (1 atm ideal gas solute state). In this case the protonation from the coordinated water molecule would be more relevant due to the stabilization of **I3b**.

## 4. Conclusion

The easily available, water-soluble *cis,mer*-[IrH $_2$ Cl(mtpms) $_3$ ] was found highly active in the selective hydrogenation of phenylacetylene to styrene in aqueous-organic biphasic reaction mixtures. Reduction of phenylacetylene could be effected by using either molecular H $_2$ , or an aqueous formic acid/Na-formate mixture, although transfer hydrogenations proceeded with somewhat lower reaction rates. Hydrogenations (with H $_2$ ) were retarded in the presence of a large excess of the alkyne substrate, while the rate of transfer hydrogenations strongly depended on the pH of the aqueous phase of the reaction mixture. Nevertheless, in

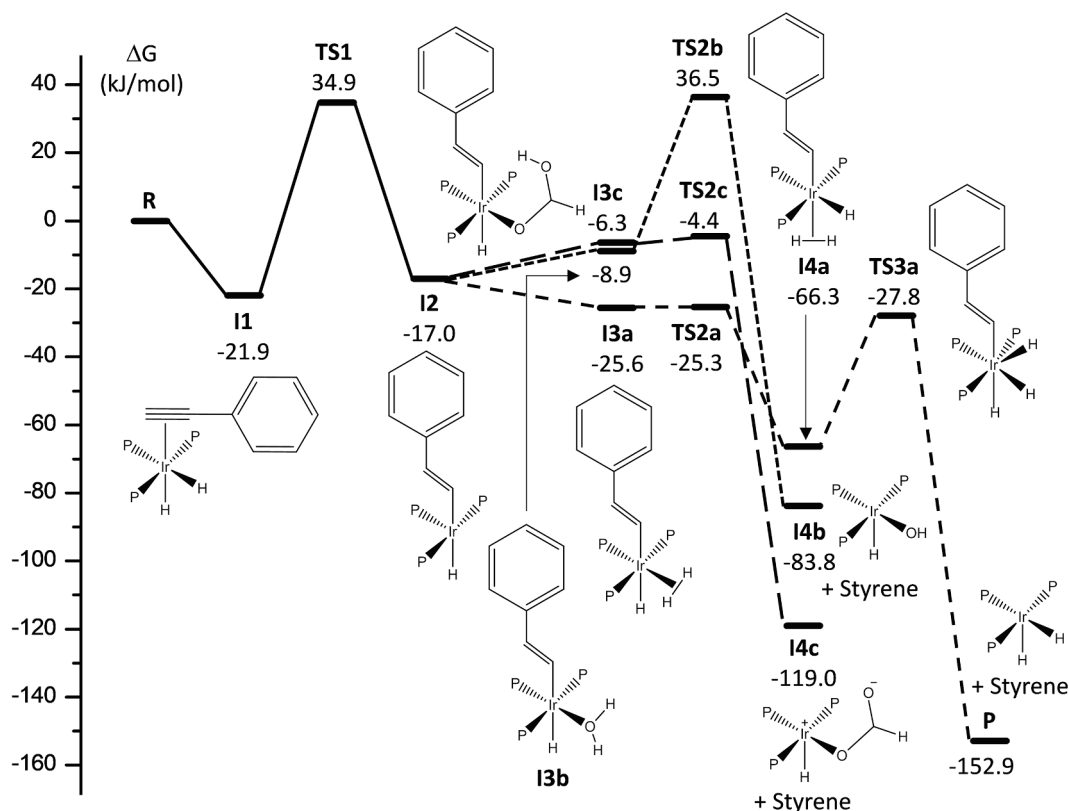


Fig. 7. The Gibbs free energy profile of the mechanism; energies are in kJ mol $^{-1}$ .

all cases, the reaction yielded exclusively styrene as product. DFT calculations were performed to identify the key species of the reaction mechanism. On the basis of both the experimental findings and the results of calculations, an unified reaction mechanism was proposed for both hydrogenation and transfer hydrogenation of alkynes with *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] as the catalyst. It is revealed, that the aqueous phase significantly contributes to the formation of the catalytically active species, *cis-mer*-[IrH<sub>2</sub>(H<sub>2</sub>O)(mtppms)<sub>3</sub>]<sup>+</sup>, presumably by strong solvation of Cl<sup>−</sup> and the complex cation resulting from chloride dissociation from *cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>].

*cis,mer*-[IrH<sub>2</sub>Cl(mtppms)<sub>3</sub>] proved to be a practical catalyst, too. It is an easily synthesized, air-stable solid, well-soluble in water. It efficiently catalyses the reduction of alkynes either by conventional hydrogenation or by hydrogen transfer from aqueous HCOOH/HCOONa, and can be simply recovered in the aqueous phase of aqueous-organic biphasic reaction mixtures.

#### CRedit authorship contribution statement

**György Hankó:** Investigation. **Richárd Márton:** Investigation. **Antal Udvardy:** Investigation, Methodology. **Mihály Purgel:** Formal analysis, Methodology, Writing - review & editing. **Ágnes Kathó:** Conceptualization, Writing - review & editing. **Ferenc Joó:** Writing - review & editing. **Gábor Papp:** Investigation, Methodology, Writing - original draft, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2021.120359>.

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