In Situ Structural Determination of a Homogeneous Ruthenium Racemization Catalyst and Its Activated Intermediates Using X-Ray Absorption Spectroscopy

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Abstract: The activation process of a known Ru-catalyst, di-carbonyl(pentaphenylcyclopentadienyl)ruthenium chloride, has been studied in detail using time resolved in situ X-ray absorption spectroscopy. The data provide bond lengths of the species involved in the process as well as information about bond formation and bond breaking. On addition of potassium tert-butoxide, the catalyst is activated and an alkoxide complex is formed. The catalyst activation proceeds via a key acyl intermediate, which gives rise to a complete structural change in the coordination environment around the Ru atom. The rate of activation for the different catalysts was found to be highly dependent on the electronic properties of the cyclopentadienyl ligand. During catalytic racemization of 1-phenylethanol a fast-dynamic equilibrium was observed.

Introduction

Knowledge about catalyst activation is crucial for the development of new catalysts and catalytic processes. When studying the activation mechanism of a transition metal complex one is often limited to indirect methods. Reaction intermediates are generally transient, but in some cases, it is possible to accumulate them for characterization by manipulating the reaction parameters. However, it is rarely possible to obtain specific bond lengths of transient metal intermediates using methods such as single-crystal X-ray diffraction.

X-ray absorption spectroscopy (XAS) is an element-specific technique used to determine the local structure around an absorbing element.[^1] Unlike single-crystal X-ray diffraction, XAS can be applied to systems in all forms of aggregation and requires only an elemental concentration in the millimolar range. In situ/operando XAS has predominantly been applied to heterogeneous catalysts, and only limited examples of homogeneous metal catalysts have been reported.[^2–7] The group of Berry utilized XAS in combination with other spectroscopic techniques to strengthen the „push–pull“ mechanism in the bi-rhodium-catalysed carbene and nitrilene transfer reactions, and this mechanism was later confirmed by the group of Fürstner.[^8] In seminal work by the group of Lei on copper-mediated cross-couplings, XAS was used to show that Cu²⁺ species were the catalytically active intermediates in the mixture, whereas Cu⁴⁺ and Cu⁵⁺ species acted as spectators.[^10,11] XAS has also been applied to other elements in attempts to elucidate catalytic species.[^5,12–16] In the few reports that exist, to the best of our knowledge, the emphasis lies either on the X-ray absorption near edge structure (XANES) in an operando setup[^17] or on accumulated intermediates[^18,19]. Alternatively, studies are performed on very simple systems with high symmetry or under conditions that do not provide time-resolved structural information of enough quality. Herein, we report an in situ XAS that allows for the structural determination of a transient metal intermediate in a ruthenium-catalysed reaction.
Metal-carbonyls are very common in modern coordination and organometallic chemistry, and they are frequently found as reagents or catalysts in organic synthesis.[20] Dicarbonyl(pentaphenylcyclopentadienyl)ruthenium chloride (1a) is formally a transfer hydrogenation catalyst, which has found numerous applications as racemization catalyst in dynamic kinetic resolution (DKR) of a wide range of alcohols.[21–27] The mechanism for the hydride transfer of alcohols with catalyst 1 and related complexes has long been a topic of discussion and dispute.[28–37] The current proposed mechanism starts with activation of the Ru chloride complex 1 by potassium tert-butoxide, to give tert-butoxide complex 3 (Scheme 1).[21,33,38] Upon the addition of a sec-alcohol, an alcohol–alkoxide exchange takes place and a new alkoxide complex 4 is formed. Since 4 is an 18-electron complex, a vacant site on Ru is required for the subsequent β-hydride elimination step, in which the hydride is abstracted from the alkoxide. This vacant site was proposed to be generated through a CO dissociation on the basis of DFT calculations,[32] and this pathway was later confirmed by 13CO exchange studies.[29] The CO dissociation enables the subsequent β-hydride elimination to occur, which gives complex Int-1 (Scheme 1). Hydride re-addition to the ketone followed by CO coordination would produce the racemic ruthenium alkoxide complex 4. Release of the alcohol through another alcohol–alkoxide exchange closes the catalytic cycle.

In an early computational work, catalyst activation and alcohol–alkoxide exchange were proposed to proceed via acyl intermediate 2a (Scheme 1).[32] In a subsequent report, experimental evidence for this intermediate acyl complex during activation of the catalyst was provided through the use of in situ FT-IR spectroscopy under cryogenic conditions.[33] Low temperature 13C NMR was consistent with the proposed acyl intermediate.[33] An XAS study of catalyst 1a and its intermediates would provide important structural information of the environment around the Ru, which has not been possible to obtain before with previous methods.

To reach this goal a temperature and stirring controlled in situ/operando reactor[40] has been applied in the present study. The in situ/operando reactor was recently successfully used to obtain structural information on in-house developed heterogeneous catalysts in operando studies.[31,42]

The aim of the present work has been to study the activation process of Ru catalysts 1a–c utilizing synchrotron radiation in an in situ XAS setup using in situ/operando reactor.

**Results and Discussion**

**In situ IR**

Activation of catalyst 1a as well as the in situ IR studies of acyl intermediate 2a have previously only been performed in toluene.[33] Tetrahydrofuran (THF), previously utilized in a DKR study with 1a,[43] is a solvent in which the metal complex 1a–c has an increased solubility. A higher concentration of the catalysts provides an increased signal to noise ratio, which is required when using the custom-made glass reactor in an in situ/operando XAS setup. Initial studies on monitoring the reaction in THF with in situ IR and 13CNMR confirmed that the structural changes follow the same pattern as those reported in toluene[33] (IR spectrum is shown in Figure 1). The main difference between the IR spectra in THF and toluene is that the lifetime of intermediate 2a (characteristic peak at 1933 cm⁻¹) is significantly prolonged in THF compared to in toluene. In toluene, full conversion to 3a took less than 5 min, whereas in THF the same reaction took about 2 h. To confirm that the reaction proceeds through the same mechanism in the two different solvents, and that THF only stabilizes intermediate complex 2a, the reaction rate was measured at varying concentrations. From these studies it became clear that the chloride abstraction follows first order kinetics (see Figure S1 and S2). The longer lifetime in THF for anion 2a compared to that in toluene.
ene can be explained by the stronger solvation of the charged intermediate by the polar THF compared to the apolar toluene. When adding the substrate, 1-phenylethanol, to the activated complex 3a, the IR signals of the carbonyls of 3a slightly blue-shifted immediately and the new complex 4a formed instantaneously (Figure S3).

In the $^{13}$C NMR recorded during the activation of catalyst 1a, the characteristic carbonyl peaks of 2a were observed in [D$_8$]THF at 209.0 and 208.3 ppm. This observation rules out the possibility that 2a is a complex formed through simple Cl$^{-}$ dissociation.

In the FT-IR spectrum of 2a in toluene [33] the acyl carbonyl peak was observed at 1596 cm$^{-1}$. The $^{13}$C NMR and the FT-IR of 2a are not compatible with two equivalent carbon monoxide ligands.

Cl$^{-}$ dissociation would in principle be possible to detect by Cl K-edge measurements. However, in light of the evidence against Cl$^{-}$ dissociation (vide infra and supra), and the fact that Cl K-edge EXAFS are not possible to perform to evaluate distances around Cl at the concentrations available in the systems under study as transmission experiments which are required for a correct interpretation, such experiments have not been performed.

**XANES**

The XANES spectra of catalyst 1a in both toluene and THF are identical, confirming that the local structure around Ru is preserved regardless of the applied solvent (see Figure S6). The K-edge was observed at 22 125 eV, determined from the first inflection point of the edge using the first derivative of the absorption edge. This observation verifies that the oxidation state of the Ru catalyst is $^{+}$II. The fact that the edge energy did not change significantly neither during the activation, nor during the catalysis suggests that the oxidation state remained unchanged during the whole process. However, a slight edge shift of 0.6 eV is shown towards lower energies upon the addition of the tBuOK, whereas this shift disappears towards reaching the activated state (see Figure S5). This slight edge shift towards lower energies can be explained by the “loss” of one CO ligand (transforms into an acyl group), therefore the decrease of electron back-donation from the ruthenium, leading to a slightly higher electron density around the metal. The XANES spectra of catalysts 1a, 1b and 1c show similar features (see Figure 2 for 1a and 1b and Figure S7 for 1c), suggesting that even though the electronic properties of the substituted cyclopentadienyl (Cp) ligand change from electron-rich to electron-deficient, the aryl groups on the Cp ligand are too far from the Ru$^{+}$ centre to influence its local geometry.

The XANES spectra showed an instantaneous change after the addition of the activator potassium tert-butoxide (tBuOK). The stronger peak around 22 135 eV showed a slight loss in intensity as well as a shift towards higher energy. However, the most noteworthy change in the XANES region is the complete disappearance of the peak around 22 160 eV after 5 min (Figure 2a, cf. spectrum 1a-0 min and 1a-5 min), which suggests considerable alteration of the environment around Ru. This peak regains its former shape after approximately 45 minutes,
after which no further change was observed in the XANES spectrum. The intensity of the peak around 22160 eV never reached that of the original catalyst. After 65 minutes, 1-phenylethanol was added, which led to no significant change of the XANES spectrum (dashed line, Figure 2a), suggesting that the local structure of complex 3a and 4a is very similar, but not necessarily identical to that of the initial catalyst 1a.

The same features in the XANES spectra were observed for catalyst 1b, although at an increased reaction rate compared to that of 1a, with no more changes being observed after ≈25 minutes (see Figure 2b). After 50 minutes, 1-phenylethanol was added (dashed line). The results show that the activation process is considerably faster when the aryl groups on the Cp ligand are changed from C6H6 to the electron-donating 4-MeO-C6H4, as in the case of 1b. On the other hand, electron-withdrawing aryl groups on the Cp ligand, as in the case of 1c, slow down the process significantly.[49] The spectra of catalyst 1c collected at 5 minutes and after 24 h after starting the activation process are almost identical (see Figure S7). The spectra at 5 minutes are almost identical for all three catalysts, implying that an intermediate state is quickly formed, which is subsequently transformed into the activated catalyst. The rate of the latter step is strongly dependent on the electronic properties of the substituted Cp ligand.

The characteristic features of XANES-spectra, and the increasing intensity of the peak at 22160 eV for catalyst 1a and 1b can be used to extract rates and to calculate the approximate half-life for the complexes during activation. Figure 3 shows the normalized intensity values measured at this energy as a function of time. From these curves, the half-life time (t1/2) of the intermediates of the activation process was obtained and found to be 28±6 and 6±0.5 minutes for catalysts 1a and 1b, respectively. Hence the activation process for 1b is almost 5 times faster than that of catalyst 1a. Note that these values are only estimated ones, as other geometrical changes also can have an effect at this energy, but as the activation mechanism is the same in all cases, they play the same role in all measurements, allowing a viable comparison. The reaction with catalyst 1a monitored by in situ IR shows a similar rate as that observed in the XANES measurements. The slight difference between the two measurements may be due to that the synchrotron irradiation changes the kinetics of the reaction.

Complex 1a dissolved in THF shows only a marginal pre-edge structural change in the XANES spectrum (see Supporting Information, Figure S9a). After addition of the activator, tBuOK, the pre-edge feature slightly shifts and becomes more distinct, indicating that the symmetry decreases around the Ru3 centre as intermediate 2a is formed. Interestingly, over time the pre-edge feature decreases again, suggesting that the activated complex 3a shows a higher symmetry than 2a. The same trend is seen for catalyst 1b (see Supporting Information, Figure S9b).

X-ray absorption fine structure (EXAFS) studies

The coordination environment of ruthenium during the course of the activation was further elucidated by analysing the EXAFS spectra. The Fourier transformed (FT) EXAFS spectra of the dissolved catalyst 1a in both THF and toluene (see Figure 4 and Figure S10, respectively), show no sign of change compared to those of the solid structure, confirming that the structure of the complex is maintained during the solvation process (Supplementary Information Table S1). When the catalyst is dissolved, its bond lengths are slightly longer than in the solid state. Notably, the distances are a bit longer in THF than in toluene, which is probably due to stronger solvation in THF as it is a more polar solvent. The FT-spectrum of the dissolved catalyst 1a in THF can be described with two distinct peaks (see Figure 4). The most distinct peak at around 1.8 Å (not phase corrected) corresponds to the interatomic distances of the 2 C atoms of the COs, the 5 C atoms of the Cp ring, and the Cl coordinated to Ru3. The refined bond lengths are 1.906, 2.240 and 2.436 Å, respectively (see Table 1). All bond lengths and their corresponding Debye–Waller coefficients are summarized in Table 1. These bond lengths agree well with previously reported single crystal data of complex 1a.[43] The second distinct peak at approximately 2.5 Å (not phase corrected) corresponds to the Ru3-O and Ru3-C-O multiple scatterings (MS) of the linear carbon monoxides. These MS events are intensified due to the focusing effect, which plays an important role when two atoms in a coordinating ligand, or part of a larger ligand, form a linear or close to linear M-L-L’ structural motif with the absorbing atom.[48,49] The refined distances for the Ru3-O of the carbonyls are 3.045 Å.

The spectra collected during the activation process of catalyst 1a are given in Figure 4a. The spectra of the catalyst were treated individually, and only representative spectra are presented in Figure 4b, whereas their refined models are presented in Table 1. It is clearly visible in the EXAFS spectra that after only 5 minutes there is an immediate and prominent change in the local structure around Ru3 (1a-5 min in Figure 4a and b) as well as an overall loss of intensity. The second main peak, in particular, exhibited a significant drop in intensity, which indicates that the number of coordinating carbon monoxides has decreased. The distinct separation between the two peaks has also disappeared, implying that a new signal has appeared...
The best fitted model contains five Ru–C distances with an average of 2.269 Å, corresponding to the Cp ring, one Ru–Cl bond with a distance of 2.346 Å, two short Ru–C bond lengths of around 2.697 Å and two Ru···O distances of around 1.859 Å (Table 1). However, the second major peak can be fitted with the MS contribution from only one CO. These distances can be interpreted in such a way that the six coordination sites around RuII are occupied by the Cp ring (hapticity of 5, three coordination sites on Ru), one Cl, one CO and one acyl ester as in intermediate 2a. The Debye–Waller factors are only somewhat larger than the values of 1a, which implies that there is one dominant species in the reaction system after 5 minutes with a very minor contribution from a second species.

The shortening of the Ru–Cl bond length from 2.44 to 2.35 Å on going from 1a to 2a is most likely due to the fact that one CO is reacted into a carboxalkoxy group (CO$_2$Bu). With this new ligand the back-donation to Ru is decreased, which leads to a significantly shorter (about 0.08 Å) Ru–Cl bond. A similar shortening effect was observed in the Ru–Cl bond length at a comparison of (S-dmso)$_3$RuCl$_3$ and O$_4$RuCl$_2$ complexes (see more detailed discussion in the Supporting Information, Tables S4a–c). Furthermore, no complex with the composition RuCl(O-ligand)(CO)(Cp) have been reported indicating the labile character of such complexes.

During the activation process, the most prominent peak centered around 1.8 Å (not phase corrected) moves towards slightly shorter distances. The second main peak, which corresponds to the CO’s, increases in intensity and the distinct separation between the two peaks reappears when the activated state 3a is reached (1a-55 min in Figure 4a and b). The main peak has shifted a few tenths of an Ångström towards shorter distances, which suggests that the chloride is lost during the activation. The best fit for the active catalyst corresponds to a coordination environment with the Cp ring, two COs, and the tert-BuO bonded to the RuII (3a), see Table 1 for the refined values.

Catalyst 1b, with an electron-donating cyclopentadienyl ring, exhibits the same spectral patterns. Since the reaction of 1b is significantly faster than that of 1a, the first spectrum collected during the activation (Figure 5, 1b-5 min) is already a mixture of species. The results of the model fitting strengthen this assumption (Supplementary Information Table S2). To obtain a good fit, the use of a mixture of possible coordinating moieties is necessary, including several factors like broken coordination numbers of the chloride ions, the carbon monoxides, the acyl group and even the tert-BuO group. The refined Debye–Waller factors are fairly large, which is consistent with a much faster reaction leading to mixed species. After the reaction had reached the activated complex 3b of catalyst 1b (Figure 5, 1b-45 min), it can be described with the exact same model as for catalyst 1a (Table S2).

It is not possible to distinguish between the two Ru–O distances. The value given is an average of the two Ru–O distances.

During the course of the synchrotron experiments, pre-catalyst 1c did not reach the active state 3c. It seems that the whole activation process is arrested at the intermediate state 2c as shown in Figure 5b. Even after 24 h there was no significant change in the structure around RuII (Figure 5b and Supplementary Information Table S3).
Substrate addition

1-Phenylethanol was added to activated complexes 3\textit{a} and 3\textit{b}, as substrate for the racemization. Following the addition, the XANES spectra of 4\textit{a} and 4\textit{b} resembled each other (Figure 2, dashed lines), as did their respective Fourier transforms (Figure 4c and inset in Figure 5a). When fitting the refined data, it becomes apparent that the hexa-coordinated structure is maintained in an octahedral configuration around Ru\textsuperscript{II} and the coordination of the Cp ring and the two CO ligands are preserved during catalysis. The last coordination site cannot be identified with certainty. It is most probably a loosely bound oxygen based on the XANES spectrum, although the EXAFS contribution is on the level of noise. The lack of clear identification of the alkoxide ligand in complex 4\textit{a}–\textit{c} suggests that the systems are in dynamic equilibria with fast interconversions of substrate molecules.

Conclusions

XAS was used to obtain detailed structural information in solution of catalysts 1\textit{a}–\textit{c}, the proposed acyl intermediates 2\textit{a}–\textit{c}, as well as the activated alkoxide complexes 3\textit{a} and 3\textit{b}. Different rates of activation were observed for the different catalysts, which was highly dependent on the electronic properties of catalysts.
the Cp ligand. In the case of 1c, the strong electron-withdrawing character of the Cp ligand inhibited the activation process. During the catalytic racemization of 1-phenylethanol, a fast-dynamic equilibrium is established between the two enantiomers of 4a–b and the ketone int-1 resulting in less resolved spectra for 4a and 4b. Therefore, only an average structure was obtained for these compounds.

Information gained from this study may aid in the development of new catalysts and to understand the different modes of activation of different catalysts.

Experimental Section

General experimental procedure

$^1$H NMR and $^{13}$C NMR were recorded at 400 MHz and 125 MHz, respectively. Chemical shifts are reported in ppm, using the residual solvent peak in CDCl$_3$ ($\delta$H 7.26 or $\delta$C 77.16) or $D_2$THF ($\delta$H 3.58 or $\delta$C 67.21) as internal standard. All solvents were dried prior to use, stored over activated 4 Å molecular sieves under 6.0 argon. Chemicals other than the catalysts were purchased from commercial sources and dried before use. Reactions were monitored using aluminium-packed plates (1.5 Å, 5 cm) which are pre-coated with silica gel (0.25 mm). UV light or KMnO$_4$ was used for visualization. Column chromatography was performed using silica gel (particle size 40–63 μm, mesh size 230–400, pore size 60 Å). Reactions at the synchrotron were performed in a glovebox under argon atmosphere. In situ IR was measured using ReactIR with a zirconium probe in a Schlenk flask which allowed easy connection with the ReactIR probe using a NS 19 fitting and the reactions were performed under 6.0 argon. Ruthenium catalysts 1a–c were prepared according to a literature procedure. Caution should be taken when distilling the dicyclopentadiene for the synthesis of the ligand for 1c.

Experimental methods XAS

The Ru K-edge EXAFS measurements of catalyst 1a in the solid state and dissolved in toluene were performed at a wiggler-based beam line 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA, operating at 3.0 GeV and 300 mA (top-up mode). The X-rays were monochromatized by a Si(220) double crystal monochromator. The second monochromator crystal was detuned to reflect 75% of the maximum intensity at the end of the scans to minimize the higher order harmonics. All the other ex situ as well as in situ spectra were collected at the undulator based P64 beam line, equipped with a Si[311] double crystal monochromator, at the Petra III Extension, Hamburg, Germany, operating at 6.0 GeV and 100 mA (top-up mode). The energy was internally calibrated in both cases with a metallic Ru foil, with the first inflection point of the K-edge spectrum assigned as 22 117 eV. For the ex situ measurements, three spectra were collected per sample and they were averaged after energy calibration, while the spectra in the in-situ measurements were treated individually. If not noted differently, the scanning rate was 5 min/scan in the –200 – 800 eV energy range around the Ru K-edge. The measurement of the solid was performed in transmission mode, whereas the solution was detected in fluorescence mode using a Lytle detector. The 1a catalyst in solid state measured at SSRL was diluted with approximately the same amount of boron nitride (BN, Merck), whereas the toluene solution was contained in a sample made of titanium frame, a Teflon spacer and 6 mm polypropylene X-ray film as windows. The measurements at Petra III were performed in a custom-made temperature-controlled reactor with a glass test tube with 1 mm thick glass walls with the beam hitting perpendicularly as possible. The measurements were performed at ambient room temperature (ca. 25 °C). The reactor is described in detail elsewhere. At Petra III, all spectra were collected in transmission mode using ion-chambers as detectors filled with appropriate gas mixtures. All data treatment (energy calibration, averaging, pre-edge subtraction, spline fitting and removal, normalization and Fourier transformation) were performed with the EXAFSPAK program package. The $k^2$-weighted experimental data were fitted by refining the structural parameters using Marquardt non-linear least-square fitting algorithm within the EXAFSPAK package. The following parameters were refined: mean interatomic distance ($R$), Debye-Waller factor coefficients ($\sigma^2$), amplitude reduction factor ($S^2$), and the threshold energy ($E$). The number of neighboring atoms were held constant during the fitting process due to strong

Figure 5. a) Fourier transform of the EXAFS spectra of catalyst 1b dissolved in THF (1b-0 min), and at 5 and 45 minutes after the addition of tBuOK (1b-5 min and 1b-45 min, respectively). The inset shows Fourier transform of the EXAFS spectra of the activated catalyst 1b (1a-45 min) and after the addition of 1-phenylethanol (1b-s). K-range 2–10 Å$^{-1}$, no phase correction ($\Delta R \approx 0.5 \text{ Å}$). b) Fourier transform of the EXAFS spectra of catalyst 1c dissolved in THF (1c-0 min), at 5 minutes and 24 hours after the addition of tBuOK (1c-5 min and 1c–24 h, respectively), k-range 2–10 Å$^{-1}$, no phase correction ($\Delta R \approx 0.5 \text{ Å}$).
correlation between the number of distances and Debye–Waller coefficients. The theoretical phases and amplitudes were calculated with the FEFF7 program.\textsuperscript{23,24} The standard deviations for the refined parameters were obtained from \(k^2\)-weighted least-squares refinements of the EXAFS function \(\chi(k)\) and did not include systematic errors of the measurements. These statistical error values allowed reasonable comparisons for example, of the significance when comparing relative shifts in distances. However, the variations in the refined parameters, including the shift in the \(E_g\) value (for which \(k = 0\)), using different models and data ranges, indicated that the absolute accuracy of the distances given for the separate complexes is within \(\pm 0.005\) to 0.02 Å for well-defined interactions. The ‘standard deviations’ given in the text have been increased accordingly to include estimated additional effects of systematic errors.

General procedure for in situ XAS

A flame dried vial was placed while hot directly into antechamber of the glovebox and placed under vacuum, then transferred into the glovebox after cooling down. Catalyst 1 (0.10 mmol) was dissolved in 1.8 mL of dry THF and the reaction vial was sealed. XAS spectra were collected on catalyst 1, the reaction vial was placed back into the glovebox and rBuOK (1 M in THF, 100 μL, 0.1 mmol) was added. The reaction vessel was placed back into the beam and the structural changes were monitored over time.

Experimental procedure for in situ IR measurement of the activation of 1a

Ruthenium catalyst 1a (203 mg, 0.32 mmol) was dissolved in 5 mL of dry THF at room temperature using a flame dried 100 mL Schlenk flask under argon and a series of spectra were recorded (2049 and 2001 cm\(^{-1}\)) before addition of rBuOK (1 M in THF, 320 μL, 0.32 mmol) and the activation was followed in an operando fashion with 15 sec scan interval. Upon addition of the rBuOK the solution turned red and the two previous CO signals disappeared, with a new dominant CO signal at 1933 cm\(^{-1}\) being observed from complex 2a. Gradually over time, the activated complex 3a could be observed with the corresponding CO signals at 2021 and 1964 cm\(^{-1}\). After the complete disappearance of 2a, the substrate, 1-phenylethanol, was added (100 μL, 0.82 mmol) and alkoxide 3a\(^{'}\) formed instantaneously without an apparent intermediate (CO peaks 2026 and 1971 cm\(^{-1}\)).

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Conflict of interest

The authors declare no conflict of interest.

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