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To cite this version:

HAL Id: hal-01710047
https://hal.umontpellier.fr/hal-01710047
Submitted on 6 Jul 2020
Metal alkyls programmed to generate metal alkylidenes by α-H abstraction: prognosis from NMR chemical shift†

Christopher P. Gordon,‡a Keishi Yamamoto,‡a Keith Searles,‡a Satoru Shirase,§ab Richard A. Andersen,‖c Odile Eisenstein‖de and Christophe Copéret‖a

Metal alkylidenes, which are key organometallic intermediates in reactions such as olefination or alkene and alkane metathesis, are typically generated from metal dialkyl compounds [M](CH2R)2 that show distinctively deshielded chemical shifts for their α-carbons. Experimental solid-state NMR measurements combined with DFT/ZORA calculations and a chemical shift tensor analysis reveal that this remarkable deshielding originates from an empty metal d-orbital oriented in the M–Cα–Cα0 plane, interacting with the Cα p-orbital lying in the same plane. This π-type interaction inscribes some alkylidene character into Cα that favors alkylidene generation via α-H abstraction. The extent of the deshielding and the anisotropy of the alkyl chemical shift tensors distinguishes [M](CH2R)2 compounds that form alkylidenes from those that do not, relating the reactivity to molecular orbitals of the respective molecules. The α-carbon chemical shifts and tensor orientations thus predict the reactivity of metal alkyl compounds towards alkylidene generation.

Introduction

Metal alkylidenes are key intermediates in many prominent chemical reactions, such as C–H activation, olefination reactions,¹ and catalytic alkene and alkane metathesis.²⁻⁴ These compounds are commonly generated by deprotonation of a metal alkyl,³ carbene transfer or α-H abstraction from [M](CH2R)2 species.⁵⁻¹¹ The latter process is particularly favoured for neopentyl (R = tBu) and related ligands, that were originally used to avoid the decomposition of these alkyl compounds via β-H transfer.¹³¹⁴ These dialkyl compounds can however decompose via α-H abstraction, an intramolecular deprotonation process between two cis-bound alkyl ligands on a metal centre, typically with d⁰ configuration, related to σ-bond metathesis (Scheme 1a).

![Scheme 1](https://example.com/scheme1.png)

(a) Alkylidene formation from [M](CH2R)2 via α-H abstraction and (b) relation between chemical shielding, chemical shift and frontier molecular orbitals.
chemist in deciding which [M][CH₂R]₂ fragment will easily generate a [M]≡CHR species via α-H abstraction and in understanding why this process occurs.

We reasoned that solid state NMR spectroscopy could be an ideal tool to probe this type of reactivity, since chemical shielding and associated $^{13}$C chemical shifts ($\delta_{iso}$ and the principal tensor components $\delta_{11} \geq \delta_{22} \geq \delta_{33}$) are directly linked to frontier molecular orbitals that control reactivity (Scheme 1b). This article reports the experimental measurement, calculation, and orbital analysis of the chemical shift tensor (CST) of the deshielded α-carbons in [M][CH₂R]₂ compounds that are prone to yield alkylidenes.

In short, we show that the occurrence of α-H abstraction from metal dialkyl compounds requires the presence of a low-lying empty metal d-orbital that points into the M–Cα–Cα’ plane. The signature of this orbital is the distinctly deshielded $^{13}$C chemical shift of the α-carbons and a specific orientation of the CST, arising from the alkylidene character on the α-carbon and polarization of the C–H bond. This situation is particularly pronounced for neopentyl ligands, explaining their propensity to generate alkylidenes via α-H abstraction.

Results and discussion

From the broad range of metal alkyl compounds that undergo α-H abstraction to yield well-defined alkylidenes or putative alkylidene species, a set of Ti and Ta compounds is selected as representative examples, chosen for historical reasons and their well-established reactivity patterns (Fig. 1). We focus on the Petasis reagent, Cp₂Ti(CH₃)₂, a well-known olefination agent involving the putative methylidene intermediate Cp₂Ti(CH₂), which is trapped as Cp₂Ti(CH₂)₂(PMe₃) in the presence of PMe₃. We also include the related compound Cp₂Ti(CH₂)₃, and the cationic alkyl compound nacnacTi(CH₂Bu)₂ (nacnac = [Ar]NC(CH₃)₂) (Ar = 2,6-(CH₂CH₃)₂C₆H₃), which generate the corresponding neopentylidene. We also prepare the d⁰ tantalum compound, TaCl(CH₂Bu)₃, an isolable intermediate in the synthesis of the first well-defined metal alkylidene, TaCl(CH₂Bu)₃(CH₂Bu), which cleanly transforms into the corresponding alkylidene TaCl(CH₂Bu)₃(CH₂Bu); analogous to the decomposition of Ta(CH₂Bu)₃ into Ta(CH₂Bu)₃(CH₂Bu). We also study Cp₂Ta(CH₂Bu)₃ and Cp₂Ta(CH₃)₃, which do not generate the corresponding alkylidenes (see Fig. 1b, red box), and the related cationic compound [Cp₂Ta(CH₃)₃][BF₄]₂. These organometallic compounds provide an experimental test to distinguish between those metal dialkyl compounds that do and those that do not form alkylidenes.

The structures of the studied metal alkyl compounds are shown in Fig. 1 and the measured and calculated chemical shift tensors are reported in Table 1. The isotropic chemical shift $\delta_{iso}$ observed in solution NMR, is the average value of the three principal tensor components ($\delta_{11} \geq \delta_{22} \geq \delta_{33}$) obtained by solid-state NMR (Scheme 1b, eqn (1)).

All of the metal alkyl compounds, with the exception of Cp₂Ta(CH₃)₃, display unusually large spins (Ω = $\delta_{11} - \delta_{33}$) for the α-alkyl carbons with deshielded $\delta_{iso}$. The low-field value of $\delta_{iso}$ is mostly due to the strongly deshielded $\delta_{11}$ component. The experimental values are compared to those obtained by DFT/ ZORA calculations (see ESIT for Computational Details), which also provide the tensor orientation. The obtained shieldings and associated chemical shifts reproduce well the experimental isotropic values and show good agreements with the individual tensor components (Table 1). The calculated shielding tensors are shown for specific examples in Fig. 2 (the tensors of the other compounds are shown in Fig. S14).

For Cp₂Ti(CH₃)₂, the most deshielded component ($\delta_{11}$) is oriented perpendicular to the plane that contains the two M–C₃ bonds (Fig. 2a). This orientation is the same as in the associated alkylidene, Cp₂Ti(CH₂) (Fig. 2b), and the isolated adduct Cp₂Ti(CH₃)(PMe₃), for which the most deshielded component is oriented perpendicular to the σ(M–C) and the π(M=C) bonds. These similarities implicate alkylidene character in the carbon atoms of the methyl groups in Cp₂Ti(CH₃)₂.

The axial carbon in the trigonal bipyramidal (TBP) molecule TaCl(CH₂Bu)₃ (Fig. 2c) has the two most deshielded tensor components $\delta_{11}$ and $\delta_{33}$ oriented perpendicular to the M–C axis, again with $\delta_{11}$ being perpendicular to the plane

Table 1 Measured α-carbon chemical shift tensors in ppm of selected metal alkyls and related alkylidenes. The calculated values are given in parenthesis

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{iso}$</th>
<th>$\delta_{11}$</th>
<th>$\delta_{22}$</th>
<th>$\delta_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂Ti(CH₃)₂</td>
<td>52 (52)</td>
<td>121 (118)</td>
<td>31 (35)</td>
<td>3 (2)</td>
</tr>
<tr>
<td>Cp₄Ti(CH₃)₄</td>
<td>50 (51)</td>
<td>100 (114)</td>
<td>30 (26)</td>
<td>22 (12)</td>
</tr>
<tr>
<td>Cp₂Ti(CH₂Bu)₂</td>
<td>98 (86)</td>
<td>193 (158)</td>
<td>70 (60)</td>
<td>31 (39)</td>
</tr>
<tr>
<td>Cp₂Ti(CH₂PMe₃)</td>
<td>286 (309)</td>
<td>714 (754)</td>
<td>82 (155)</td>
<td>70 (17)</td>
</tr>
<tr>
<td>nacnacTi(CH₂Bu)₂</td>
<td>143 (139)</td>
<td>217 (212)</td>
<td>184 (175)</td>
<td>28 (30)</td>
</tr>
<tr>
<td>nacnacTi(CH₂Bu)(OTf)</td>
<td>271 (277)</td>
<td>569 (613)</td>
<td>271 (265)</td>
<td>–28 (−47)</td>
</tr>
<tr>
<td>Ti(CH₂Bu)₄</td>
<td>119 (118)</td>
<td>165 (158)</td>
<td>137 (148)</td>
<td>55 (49)</td>
</tr>
<tr>
<td>TaCl(CH₂Bu)₃</td>
<td>135 (142)</td>
<td>214 (214)</td>
<td>149 (147)</td>
<td>43 (64)</td>
</tr>
<tr>
<td>TaCl(CH₂Bu)₄</td>
<td>113 (126)</td>
<td>154 (159)</td>
<td>146 (162)</td>
<td>40 (58)</td>
</tr>
<tr>
<td>TaCl(CH₂Bu)(CH₂Bu)</td>
<td>251 (264)</td>
<td>––</td>
<td>––</td>
<td>––</td>
</tr>
<tr>
<td>TaCl(CH₂Bu)₃</td>
<td>115 (130)</td>
<td>156 (171)</td>
<td>141 (152)</td>
<td>48 (65)</td>
</tr>
<tr>
<td>Cp₂Ta(CH₃)₃</td>
<td>25 (22)</td>
<td>43 (37)</td>
<td>28 (33)</td>
<td>4 (–4)</td>
</tr>
<tr>
<td>Cp₂Ta(CH₃)₄</td>
<td>22 (23)</td>
<td>48 (49)</td>
<td>19 (15)</td>
<td>–1 (–7)</td>
</tr>
<tr>
<td>[Cp₂Ta(CH₃)₃][BF₄]₂</td>
<td>57 (62)</td>
<td>172 (164)</td>
<td>24 (42)</td>
<td>–27 (–20)</td>
</tr>
</tbody>
</table>

* Axial, † Equatorial, ‡ External and § Internal carbons. † Not measured.
For carbon p-orbitals, deshielding along direction i occurs when the vacant and occupied orbitals are oriented perpendicular to each other and to the i-axis.

The individual orbital contributions to the most deshielded component of the CST (\(\delta_{11}/\sigma_{11}\)), obtained through a Natural Chemical Shift (NCS) analysis of the representative examples, C\textsubscript{p}2Ti(CH\textsubscript{3})\textsubscript{2} and TaCl(CH\textsubscript{2}Bu)\textsubscript{4}, and the associated alkylidenes are plotted in Fig. 3 (values given in Table S4†). Notably, the largest contribution to deshielding in the \(\delta_{11}/\sigma_{11}\) component of the metal alkyl compounds is always associated with the \(\sigma(M-C_{\text{ads}})\) bond, as found for the corresponding metal alkylidenes.

The large deshielding of the z-carbons, originating from the \(\sigma(M-C_{\text{ads}})\) bond, indicates the presence of a low-lying vacant orbital that is oriented perpendicular to the M–C axis and the direction of the deshielding. The emergence of this low-lying empty orbital is due to the weak \(\pi\)-donating ability of alkyl groups that, by interaction with an empty d\textsubscript{π} metal orbital, develop a \(\pi\)-interaction by which the M–CH\textsubscript{3}R bond acquires alkylidene character, as shown for C\textsubscript{p}2Ti(CH\textsubscript{3})\textsubscript{2} in Fig. 4c; this orbital is labelled as \(\pi(M-C)\) orbital, which is the LUMO of the compound (Fig. 4c right and S15†), is responsible for the observed deshielding by coupling with the occupied \(\sigma(M-C)\) orbital (Fig. 4a). In the corresponding alkylidene C\textsubscript{p}2Ti(CH\textsubscript{3})\textsubscript{2}, there is a smaller energy gap between the \(\sigma(M=C)\) and \(\pi^*(M=C)\) orbitals, hence a significantly larger deshielding (Fig. 4b). Similarly, in TaCl(CH\textsubscript{2}Bu)\textsubscript{4}, the largest part of the deshielding on the axial z-carbon originates from the occupied \(\sigma(M–C)\) orbital (Fig. 4d left), which is coupled to the vacant \(\pi^*(M–C)\) orbital (Fig. 4d right), again evidencing a \(\pi\)-type interaction of the metal atom with the alkyl ligand. The larger deshielding of the axial carbon atom as compared to the equatorial carbon atoms indicates larger \(\pi\)-character in the former M–C bond.

A similar pattern and analysis applies to C\textsubscript{p}tBu, C\textsubscript{p}2Ti(CH\textsubscript{2}Bu)\textsubscript{2}, nacnacTi(CH\textsubscript{2}Bu)\textsubscript{2}+, and Ti(CH\textsubscript{2}Bu)\textsubscript{4}, where deshielding of the z-carbon mostly arises from the \(\sigma(M-C)\) bond, indicating a low-lying orbital of \(\pi^*(M–C)\) character, oriented perpendicular to the \(\sigma(M–C)\) bond (Table S4 and

containing two M–C\textsubscript{ads} bonds, while the most shielded component \(\delta_{13}\) is along the M–C axis. The orientation of the tensor in this compound is similar to that of the associated alkylidene (Fig. 2d). It should be noted that TaCl(CH\textsubscript{2}Bu)\textsubscript{4} shows two distinct signals in the solution NMR at 144 and 116 ppm in a 1 : 3 ratio, corresponding to axial and equatorial CH\textsubscript{2}Bu groups, while the most shielded (159 ppm) stands out by a notably large span (Table S1†). In solid-state NMR, the situation is complicated by the presence of several sites in the powdered sample. At 100 K, six distinct sites are observed in a chemical shift range of 113 to 135 ppm (the extreme values are reported in Table 1, for other values see Table S1†). The most deshielded site (135 ppm) stands out by a notably large span (\(\Omega = 171\) ppm) and is tentatively assigned to the axial carbon, while the other sites show spans (\(\Omega\)) that vary between 102 and 143 ppm and presumably correspond to equatorial z-carbons in different environments. DFT calculations also show that the axial z-carbon is strongly deshielded (\(\delta_{111}/\delta_{11} = 142/214\) ppm), while the equatorial carbons are more shielded (\(\delta_{111} = 126–129\) ppm, \(\delta_{11} = 159–189\) ppm). The calculations show the presence of several local minima upon rotation of the axial CH\textsubscript{2}Bu ligand in TaCl(CH\textsubscript{2}Bu)\textsubscript{4}, giving rise to an ensemble of conformations as a possible explanation for the observation of several peaks.

The origin of the deshielded chemical shift values is investigated by an orbital analysis of the corresponding shielding tensor (\(\sigma, \text{ eqn (2)}\)).\textsuperscript{15} Decomposition of the shielding into diamagnetic (\(\sigma_{\text{dia}}\)) and paramagnetic contributions, which also include contributions from spin–orbit coupling (\(\sigma_{\text{para SO}}\), eqn (3)), reveals that the variation in the shielding values is mostly associated with \(\sigma_{\text{para SO}}\). For the compounds investigated here, spin–orbit coupling is relatively small (Table S7†), allowing for interpreting \(\sigma_{\text{para SO}}\) based solely on the paramagnetic contributions. These originate from the magnetically induced coupling of excited electronic states with the ground state, by action of the angular momentum operator \(L_i\) (eqn (4)). Hence, the chemical shift is sensitive to the relative energy and orientation of the frontier orbitals, establishing a link to reactivity.
Fig. S11†). The emergence of this orbital requires an empty metal d-orbital in the M–C–\( \alpha \) plane of the correct symmetry to interact with the p\( \alpha \)-orbital of the alkyl ligand. Such an orbital is indeed present in all the aforementioned bis-alkyl compounds that generate alkylidenes via x-H abstraction (Fig. S15†). Thus, the deshielding is a signature of alkylidene character in the metal–carbon bond.

The metal neopentyl compounds show particularly low \( J_{C-H} \) coupling constants (e.g. 116 Hz for Cp\(_2\)Ti(CH\(_2\))\(_2\)Bu\(_2\), 105 Hz and 110 Hz for the two x-carbons in nacnacTi(CH\(_2\)Bu\(_2\))\(_2\)), 110 Hz in Ti(CH\(_2\)Bu\(_2\))\(_4\), and 96 Hz for the axial carbon in TaCl(CH\(_2\)Bu\(_2\))\(_4\)). This effect is slightly less pronounced in Cp\(^*\)\(_2\)TiMe\(_2\) (122 Hz average coupling constant). These lowered coupling constants indicate more p-orbital character in the C–H bonds, an additional signature of a \( \pi(M-C) \) type interaction. Notably, the equatorial carbons in TaCl(CH\(_2\)Bu\(_2\))\(_4\) show a larger \( J_{C-H} \) coupling constant (115 Hz) than the axial carbon (96 Hz), indicating a less developed \( \pi \)-interaction in the former, in line with the less deshielded carbon atoms.

The formation of alkylidenes from bis-alkyl complexes via x-H abstraction requires the presence of a low-lying empty orbital in the plane of the M–C\(_\alpha\) and M–C\(_\alpha\) bonds. While the deshielded chemical shift value and large anisotropy of the CST indicate the presence of such an orbital, the CST orientation probes the location of this empty orbital. For example, TaCl\(_2\)(CH\(_2\)Bu\(_2\))\(_4\) features a trigonal-bipyramidal geometry with two Cl-ligands in axial positions. The rather large deshielding on the x-carbon (115 ppm) indicates a low-lying empty orbital, but the most deshielded component (\( \delta_{11} \)) of the CST is not perpendicular to a plane containing two equatorial Ta–C\(_\alpha\) bonds but rather perpendicular to the plane containing an equatorial Ta–C\(_\alpha\) and an axial Ta–Cl bond, which is also the plane containing the LUMO (Fig. 4e). Accordingly, the alkylidene character is not developed in the direction needed for x-H abstraction. This compound is therefore stable, even when heated to 100 °C in the presence of PMe\(_3\) for 4 h, in contrast to TaCl(CH\(_2\)Bu\(_2\))\(_4\). In other words, in a trigonal-bipyramidal structure, x-H abstraction is favoured between an axial and an equatorial alkyl ligand and is not readily accessible in TaCl\(_2\)(CH\(_2\)Bu\(_2\))\(_4\), where both axial positions are occupied by Cl-ligands.

The importance of the presence of a vacant metal d-orbital with the appropriate orientation for the observed deshielding is further demonstrated by comparing Cp\(^*\)\(_2\)Ti(CH\(_2\))\(_2\)Bu\(_2\), Cp\(_2\)Ta(CH\(_2\))\(_2\)Bu\(_2\), and Cp\(_2\)Ta(CH\(_2\))\(_3\)\(^+\). While Cp\(^*\)\(_2\)Ti(CH\(_2\))\(_2\) and Cp\(_2\)Ta(CH\(_2\))\(_2\)\(^+\) both show rather deshielded and anisotropic x-carbons, the NMR signatures of Cp\(_2\)Ta(CH\(_2\))\(_3\) are markedly different (Fig. 5). The chemical shift drops from 52 ppm in Cp\(_2\)Ta(CH\(_2\))\(_2\) to 22 and 25 ppm in Cp\(_2\)Ta(CH\(_3\))\(_3\) (external and internal carbons, respectively), mostly originating from a large decrease of the \( \delta_{11} \) component (121 ppm in Cp\(_2\)Ti(CH\(_3\))\(_2\) as compared to <50 ppm for Cp\(_2\)Ta(CH\(_3\))\(_3\)). The third methyl-substituent in Cp\(_2\)Ta(CH\(_3\))\(_3\) interacts with the empty metal orbital that is required for developing the alkylidene character (the remaining empty orbitals on the metal, which are involved in bonding with the Cp rings, are too high in energy for such an interaction). However, abstraction of a methyl-ligand generates Cp\(_2\)Ta(CH\(_3\))\(_2\)\(^+\), isoelectronic to Cp\(_2\)Ti(CH\(_3\))\(_2\), and restores the highly anisotropic CST and deshielded chemical shift values (Fig. 5 and Table 1).

The nature of the alkyl ligands also plays an important role in manipulating the alkylidene character on the x-carbon. This is illustrated by comparing the bis-neopentyl metallocone, Cp\(_2\)Ti(CH\(_2\)Bu\(_2\))\(_2\) with the bis-methyl metallocones, Cp\(_2\)Ti(CH\(_3\))\(_2\) and Cp\(^*\)\(_2\)Ti(CH\(_3\))\(_2\), since detailed kinetic data on the decomposition via x-H abstraction is available for the latter metallocone.\(^{27}\) Cp\(_2\)Ti(CH\(_2\)Bu\(_2\))\(_2\) displays a much more deshielded and anisotropic x-carbon, due to the coupling of \( \pi(M-C) \) with \( \pi^*(M-C) \), in addition to a significant contribution of the coupling of \( \sigma(C_\alpha-C_\beta) \) and \( \pi^*(M-C_\alpha) \) (Table S4 and Fig. S11†). The contribution of \( \sigma(C_\alpha-C_\beta) \) is associated with the wide calculated \( \alpha(M-C_\alpha-C_\beta) \) angle of 136°, signalling the increased alkylidene character in the Ti–C bond. The NMR data thus suggest a lower
been reported on the elimination of CH₃tBu from Ti(CH₂tBu)₄ and Ta(CH₂tBu)₅. Both compounds follow first order kinetics for α-H abstraction. For Ti(CH₂tBu)₄, values of ΔG° = 26.4 kcal mol⁻¹ and kₐ/ₚ = 5.2 ± 0.4 were found. For Ta(CH₂tBu)₅, the values were ΔG° = 22.3 kcal mol⁻¹ and kₐ/ₚ = 14.1 ± 0.8 (note that ΔG° was determined for the deuterated compound).

It is important to note the close analogy between alkylidenic character of the M–C bond and the occurrence of what is referred to as α-H agostic interactions. α-H Agostic interactions are evidenced by acute M–C–H angles (<109.47°) and are generally associated with low J_C-H coupling constants for the carbon bound to the metal (<125 Hz). The presence of an α-H agostic interaction is associated with a π-type interaction of a p-orbital on the α-carbon with a vacant metal d-orbital, resulting in the observed geometrical features and lower J_C-H coupling constants. Thus, an α-H agostic interaction is also an indirect reporter of an alkylidenic character in a M–C bond. However, the CST values that signal alkylidenic character can be present in the absence of geometrical features or lowered J_C-H coupling constants associated with α-H agostic interactions. For example, in TaCl(CH₂tBu)₄, one M–C–H bond angle at the axial carbon is calculated to be 95° (which can be considered agnostic), whereas, in Cp₂Ti(CH₂CH₃)₂, the M–C–H angles are calculated to be 112.7° (the H atom in the σ₈ plane) and 109.7° (the H atom out of σ₈ plane). While both TaCl(CH₂tBu)₄ and Cp₂Ti(CH₂CH₃)₂ have alkylidenic character, as evidenced by their CSTs, only the former is considered to be α-C–H agostic based on its calculated structure. Our view is that an α-C–H agostic interaction is better described as a π-donation from the carbon p-orbital, rather than as a 3-center-2-electron bond. The philosophical question remains: is the M–H–C₈ interaction due to the alkylidenic character of the carbon atom bound to the metal, or does the alkylidenic character arise from the M…H–C₈ interaction? Perhaps a distinction without a difference.

**Conclusions**

In summary, strongly deshielded chemical shift values of the α-carbons in [M(CH₂R)]₂ compounds in combination with a large anisotropy and specific orientation of the chemical shift tensor reveal the presence and location of low-lying empty metal d-orbitals. The alkylidenic character in the M–CH₂R bond activates the α-C–H bond towards α-H abstraction when the low-lying empty orbital is appropriately oriented. While this orbital arrangement can lead to the development of an α-C–H “agnostic” interaction, the magnitude and orientation of the CST is a much more unequivocal signature of the alkylidenic character of the M–C bond. The CST shows that the parent alkyl compounds already contain inscribed information about the reaction products and are programmed to evolve into metal alkylides, a situation particularly favoured for neopentyl-type ligands. While this study has focused on Ti and Ta d⁰ compounds, the associated principle is likely applicable to a wide range of metal alkyls with low d-electron counts. The theme of this article is that NMR chemical shift values of atoms directly bonded to a metal centre provide information about the electronic
structure and are powerful reporters of the location, orientation, and relative energy of the frontier molecular orbitals. This study shows that chemical shifts can be of predictive value of a compound’s reactivity, making their physical interpretation an invaluable tool for the development and the understanding of mechanisms and reactivity. We are currently further exploring this connection.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

CPG and KS are supported by SNF grant number 2000201_169134 and 200020_149704. CPG is a recipient of the Scholarship Fund of the Swiss Chemical Industry. KY thanks the Canon foundation for a post-doctoral fellowship and the Murata Overseas Scholarship for Overseas Research Activities 2017. SS thanks the Osaka University Scholarship for Overseas Research Activities 2017. OE was partially supported by the Research Council of Norway through its Centres of Excellence scheme, project number 262695.

**Notes and references**


