NMR chemical shift analysis decodes olefin oligo- and polymerization activity of d⁰ group 4 metal complexes

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Edited by Tobin J. Marks, Northwestern University, Evanston, IL, and approved May 16, 2018 (received for review February 24, 2018)

Oligomerization and polymerization processes are highly active fields of research (1–5) and at the heart of the petrochemical industry, producing α-olefins and polyolefins, respectively, that are some of the most important commodity chemicals and polymers (6). In polymerization, the coordination and insertion of an olefin into a metal–carbon bond, referred to as the Cossee–Arlmann and Green–Rooney polymerization mechanisms. The 13C NMR chemical shifts, the α-H agostic interaction, and the low activation barrier of olefin insertion are, therefore, the results of the same orbital interactions, thus establishing chemical shift tensors as a descriptor for olefin insertion.

Olefin polymerization | olefin oligomerization | NMR spectroscopy | chemical shift tensor analysis | frontier molecular orbitals

The rational understanding and design of catalysts pose major challenges to chemists. While catalysts are involved in around 90% of industrial chemical processes, their discovery and development are usually based on screening and serendipity. Here, we show through a detailed analysis of the NMR chemical shift that the activity of olefin polymerization and oligomerization catalysts is directly related to the chemical shift of the carbon atom bound to the metal center. This relation is traced to specific frontier molecular orbitals, which induce π-character in the metal–alkyl bond, thereby favoring insertion. This result not only reveals a surprising analogy between olefin polymerization and metathesis, but also establishes chemical shift as a predictive descriptor for catalytic activity in these industrially relevant processes.

Significance


The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1803382115/-/DCSupplemental.

www.pnas.org/cgi/doi/10.1073/pnas.1803382115
bon bond, which results from the interaction of the symmetry. This partial group with an empty metal d-orbital of low energy and appropriate reactions to olefin metathesis.

A

B

C

D

Fig. 1. Proposed mechanisms for olefin insertion involving electrophilic metal centers: (A) Cossee-Arltman mechanism, (B) Green-Rooney mechanism, and (C) modified Green-Rooney mechanism. (D) Typical olefin polymerization catalysts (M = Ti, Zr, Hf) (13, 28–35).

information about the nature of the metal–carbon chemical bond and associated reactivity (57–62). We thus reasoned that a chemical shift analysis based on a combined experimental and computational approach would be a valuable tool to probe the electronic structure of reaction intermediates in polymerization and oligomerization processes and to identify key requirements that differentiate between active and inactive catalysts or between dimerization and trimerization catalysts. In this article, we show that the NMR CSTs of the α-carbon in compounds that undergo olefin insertion and ring expansion are diagnostic of their reactivity. They provide signatures for the presence of alkylidenic character in the metal–carbon bond, which results from the interaction of the π-donor alky group with an empty metal d-orbital of low energy and appropriate symmetry. This partial π-bond character is an essential ingredient for insertion and ring expansion steps found in both olefin polymerization and oligomerization processes involving group 4 metal complexes. This indicates that olefin insertion and ring expansion can be viewed as [2 + 2]-cycloaddition reactions, thus relating these reactions to olefin metathesis.

Results

Measurement and Calculation of CSTs. The following organometallic compounds are prepared and characterized by solid-state NMR: the olefin polymerization precatalysts Cp2MeCl (M = Ti, Zr, and Hf) (63) as well as the cationic species [Cp2ZrMe(thf)][BF4]– (64) as a model compound for ethylene polymerization catalysts. We use the two-component zero-order regular approximation (ZORA) combined with density functional theory (DFT) to analyze the shielding tensors of Cp2MRCl (R = Et) and the cationic species Cp2MR+ (M = Ti, Zr, and Hf; R = Me, Et, and Bu) as well as selected ethylene adducts Cp2MR(C2H4)+ and isolable thf adducts Cp2MR(thf)+ (Fig. 3A). For compounds with β-hydrogens, both the α-agostic and β-agostic structures are calculated (SI Appendix, Computational Details).

For the investigation of oligomerization processes, the relevant olefin complexes and metallacycloalkanes are calculated [Cp2M(C2H6), Cp2M(C2H5)2, and Cp2M(C4H8)] (M = Ti, Zr, and Hf) as well as the cationic oligomerization intermediates Cp[η2-Ar]Ti(C2H4)+, Cp[η2-Ar]Ti(C6H12)+, and Cp[η2-Ar]Ti(C6H5)2+ (Fig. 3B). The solid-state NMR spectra of the model compounds [(C5Me3)2Ti(C2H4)] and Cp2Zr(C2H4) are also measured experimentally.

The chemical shifts (δiso, δ11, δ22, δ33) for all analyzed Zr-based compounds related to olefin polymerization are shown in Table 1 along with selected Ti and Hf derivatives. The data for Ti-based compounds related to olefin oligomerization and selected Zr compounds are summarized in Table 2. Good agreement between calculated and experimental values is obtained when data are available. A complete list of all calculated compounds is found in SI Appendix, Table S1.

Although many computational studies have been carried out on these complexes and their role in oligo- and polymerization reactions (67–83), the electronic structures and relative energies of relevant reactants, intermediates, and transition states are computed with the same method used for optimizing the geometries for NMR calculations for consistency.

Development of the CST Along Reaction Pathways.

Olefin polymerization. This subsection focuses on Zr-based olefin polymerization catalysts. The CST of analogous Ti and Hf compounds follows a similar trend, with the Ti compounds having the most deshielded values (SI Appendix, Figs. S1 and S2). The development of the CST during ethylene polymerization is summarized in Fig. 4A. The most significant changes of the CST are associated with the most deshielded δ11 component, which is oriented perpendicular to the σ plane for all of the aforementioned compounds.

The δ11 component is moderately deshielded in Cp2ZrEt2I (δ11 = 102 ppm). The calculations show that, on abstraction of the Cl− ligand, Cp2ZrEt2I can exist in both a β-H agostic structure and an α-H agostic structure. The β-H agostic compound is calculated to be preferred by around 4.5 kcal mol−1, in agreement with previous studies (68–71). Since olefin insertion into metal–carbon bonds has been proposed to be assisted by an α-H agostic interaction, in the ground and/or the transition state (24, 26, 70, 71), we calculate both the α- and β-H agostic complexes and the associated transition states for insertion. Ethylene coordination and the transition state for insertion are more favorable for the α-H agostic Cp2ZrEt2I∗ (ΔG = −3.6 kcal mol−1).

Fig. 2. (A) Proposed metallacycle mechanism of olefin oligomerization with early transition metals, (B) catalyst for the dimerization of ethylene and Zr-based model systems, and (C) selected catalysts for the trimerization of ethylene.
and $\Delta G^2 = 1.4$ kcal mol$^{-1}$) relative to the $\beta$-H agostic $\text{Cp}_2\text{ZrEt}^+$ ($\Delta G = 6.0$ kcal mol$^{-1}$ and $\Delta G^2 = 9.1$ kcal mol$^{-1}$). The more favorable calculated pathway found for the $\alpha$-H agostic compound suggests that this intermediate is the reactive state of the catalyst, while the $\beta$-H agostic $\text{Cp}_2\text{ZrEt}^+$ complex is the resting state, which is in accordance with previous studies (70, 71).

Compared with $\text{Cp}_2\text{ZrEtCl}$, the $\delta_{11}$ component of $\text{Cp}_2\text{ZrEt}^+$ is more deshielded in both the $\beta$-H and $\alpha$-H agostic structures, but this effect is much more pronounced in the latter (Fig. 4A). On ethylene coordination, the development of the CST in the two structures diverges: the $\delta_{11}$ component becomes significantly more shielded in the $\beta$-H agostic structure, leading to a more isotropic CST, while the $\delta_{11}$ component becomes even more deshielded for the $\alpha$-H agostic structure, generating a highly anisotropic CST. The corresponding $\beta$-H and $\alpha$-H agostic butyl complexes $\text{Cp}_2\text{ZrBu}^+$ show very similar tensors to those in $\text{Cp}_2\text{ZrEt}^+$, indicating that the foregoing analysis applies to the first and second insertion steps and, to all stages of the polymerization process. Notably, ethylene insertion into the metal-alkyl complex leads to a migration of the alkyl chain to the adjacent site, while keeping alkylidene character on the $\alpha$-carbon. This is particularly evident for the $\alpha$-H agostic complex, which is consistent with polymer-chain growth with the alternating coordination site at each insertion step; this is of key importance to explain stereoselectivity in the polymerization process (84).

**Olef in oligomerization.**

The development of the CST during ethylene oligomerization is illustrated in Fig. 4B for both the neutral $\text{Cp}_2\text{Ti}$- and the cationic $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)^+$-based systems. Again, it is apparent that the most significant changes of the CST are associated with the $\delta_{11}$ component, which is oriented similarly in the studied compounds (perpendicular to the $\sigma$ plane) (Fig. 4B). This component is highly deshielded for $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_4)$, which inserts an olefin with a moderate Gibbs energy of activation, forming the corresponding metallocyclopentane ($\Delta G = 13.4$ kcal mol$^{-1}$ for the formation of the bis-ethylene adduct and $\Delta G^2 = 8.0$ kcal mol$^{-1}$ for metallocyclopentane formation). While $\delta_{11}$ is similar for the ethylene carbon in $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_4)$ and free ethylene (Table 2), the shape of the associated tensors is different as shown by the different values of the $\delta_{32}$ component that are 41 and 124 ppm for $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_4)$ and $\text{C}_2\text{H}_4$, respectively. In the corresponding bis-ethylene adduct $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_4)_2$ and metallocyclopentane $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_6)_2$, the $\delta_{11}$ component is much more shielded, giving rise to only moderately anisotropic CSTs, which is also true for the corresponding metallocycloheptane. The latter molecule is, however, not detected experimentally, since no ethylene insertion is observed in $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_6)$. Similar observations are made for the corresponding $\text{Zr}$- and $\text{Hf}$-based systems (SI Appendix, Figs. S3 and S4).

In sharp contrast to $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_4)_2$ and $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_6)_2$, the analogous cationic bis-ethylene complex $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)_2$ and metallocyclopentane $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)^+$, which are proposed intermediates in the ethylene trimerization process (77–80), show a large deshielding on the $\alpha$-carbons associated with a strongly deshielded $\delta_{11}$ component, giving rise to strongly anisotropic CSTs. The corresponding metallocycloheptane $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_6)^+$, formed after insertion of an ethylene molecule into the metal-carbon bond of $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)^+$, also shows a deshielded $\delta_{11}$ component, albeit less pronounced in comparison with the metallocyclopentane $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)^+$.

The larger deshielding in $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)_2$ and $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_6)_2$ compared with $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_4)_2$ and $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_6)_2$ corresponds to an energetically more accessible metallocyclopentane and metallocycloheptane formation in the reaction with ethylene. The calculated Gibbs energies of activation are $\Delta G^1 = +5.5$ and +8.0 kcal mol$^{-1}$ for metallocyclopentane formation from $\text{Cp}(\eta^5-\text{Ar})\text{Ti}(\text{C}_2\text{H}_4)^+$ and $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_6)_2$, respectively, and $\Delta G^2 = +15.5$ and +51.0 kcal mol$^{-1}$ for the associated metallocycloheptane formation, respectively.

### Table 1. 13C NMR chemical shifts ($\delta_{iso}$, $\delta_{11}$, $\delta_{32}$, $\delta_{33}$) of $\alpha$-carbons of selected compounds relevant for olefin polymerization processes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{iso}$</th>
<th>$\delta_{11}$</th>
<th>$\delta_{32}$</th>
<th>$\delta_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cp}_2\text{TiCl}$</td>
<td>66 (69)</td>
<td>132 (134)</td>
<td>51 (48)</td>
<td>11 (25)</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrEtCl}$</td>
<td>49 (50)</td>
<td>98 (102)</td>
<td>38 (35)</td>
<td>10 (13)</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{HfEtCl}$</td>
<td>46 (53)</td>
<td>100 (108)</td>
<td>21 (35)</td>
<td>17 (16)</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrMe}$</td>
<td>(101)</td>
<td>(256)</td>
<td>(63)</td>
<td>(−15)</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrMe(thf)}^+$</td>
<td>38 (51)</td>
<td>104 (134)</td>
<td>20 (30)</td>
<td>−10 (−11)</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrEt}^{\beta}$</td>
<td>61* (73)</td>
<td>192 (33)</td>
<td>(3)</td>
<td>(−7)</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrEt}^{\alpha}$</td>
<td>147 (325)</td>
<td>107 (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrBu}^{\beta}$</td>
<td>76 (192)</td>
<td>44 (7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrBu}^{\alpha}$</td>
<td>155 (332)</td>
<td>112 (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrEt}(\text{C}_2\text{H}_4)^{\beta}$</td>
<td>36 (74)</td>
<td>31 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrEt}(\text{C}_2\text{H}_4)^{\alpha}$</td>
<td>172 (406)</td>
<td>93 (12)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reported value for [(C$_5$H$_4$Me)$_2$Zr(thf)]$[\text{BPh}_4]$ is in ref. 65.
due to paramagnetic contributions, which also lead to the large deshielding of the $\delta_{11}$ component. The paramagnetic contributions to deshielding originate from the magnetically induced coupling of excited electronic states with the ground state by action of the angular momentum operator $\hat{L}_i$ ($i = 1 \rightarrow 3$) (Fig. 5A, equation 3). Hence, chemical shift is sensitive to the relative energy and orientation of frontier orbitals, thus establishing a link to molecular reactivity. For atomic carbon p-orbitals, deshielding by $\hat{L}_i$ arises when the vacant and occupied orbitals are oriented perpendicular to each other and to the $i$ axis as schematically illustrated for the case of ethylene (Fig. 5B).

Table 2. $^{13}$C NMR chemical shifts ($\delta_{iso}$, $\delta_{11}$, $\delta_{22}$, $\delta_{33}$) of $\alpha$-carbons of selected compounds relevant for olefin oligomerization processes.

<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>Cp$_2$Ti(C$_2$H$_4$)</td>
<td>(102)</td>
<td>(258)</td>
<td>(41)</td>
<td>(8)</td>
</tr>
<tr>
<td>(Cp*)$_2$Ti(C$_2$H$_4$)</td>
<td>104 (101)</td>
<td>246 (248)</td>
<td>32 (44)</td>
<td>32 (11)</td>
</tr>
<tr>
<td>(Cp)$_2$Ti(C$_2$H$_2$)$_2$</td>
<td>(57)</td>
<td>(97)</td>
<td>(61)</td>
<td>(15)</td>
</tr>
<tr>
<td>Cp$_2$Ti(C$_2$H$_3$)</td>
<td>(66)</td>
<td>(131)</td>
<td>(53)</td>
<td>(13)</td>
</tr>
<tr>
<td>Cp$_2$Ti(C$_2$H$_4$)</td>
<td>(75)</td>
<td>(142)</td>
<td>(59)</td>
<td>(25)</td>
</tr>
<tr>
<td>Cp$_2$Zr(C$_2$H$_4$)</td>
<td>(87)</td>
<td>(235)</td>
<td>(30)</td>
<td>(5)</td>
</tr>
<tr>
<td>Cp$_2$Zr(C$_2$H$_8$)</td>
<td>40 (46)</td>
<td>83 (99)</td>
<td>35 (38)</td>
<td>3 (1)</td>
</tr>
<tr>
<td>Cp$_2$Zr(C$_4$H$_8$)</td>
<td>(89)</td>
<td>(215)</td>
<td>(90)</td>
<td>(46)</td>
</tr>
<tr>
<td>Cp$_2$Zr(C$_6$H$_12$)</td>
<td>(122)</td>
<td>(235)</td>
<td>(100)</td>
<td>(33)</td>
</tr>
<tr>
<td>Cp$_2$Zr(C$_4$H$_8$)</td>
<td>(115)</td>
<td>(200)</td>
<td>(99)</td>
<td>(46)</td>
</tr>
</tbody>
</table>

*Reported in ref. 66.

Calculated values are given in parentheses. All values are given in parts per million.

To understand the observed deshielding of the carbon chemical shift in the metal-alkyl compounds at the frontier orbital level, the shielding tensors of representative compounds are analyzed by an orbital analysis, closely related to the Natural Chemical Shift (NCS) analysis (87, 96, 113). We focus on the $\delta_{11}$ component, since this component has the largest influence and is mostly responsible for the observed trends (the NCS analyses for all components are given in SI Appendix).

**Olefin polymerization.** The CST values given in this subsection focus on the species derived from the Cp$_2$Zr fragment, but the general findings also apply to the isoelectronic Ti and Hf systems (SI Appendix). The orbital analysis reveals that deshielding of the $\delta_{11}$ component in Cp$_2$ZrEtCl, Cp$_2$ZrMe$_2$, Cp$_2$ZrEt$^+$, Cp$_2$ZrEt(C$_2$H$_4$)$_2^+$, and Cp$_2$ZrBu$^+$ mainly arises from the contribution of the $\sigma$(M–C) bond to the paramagnetic component of $\delta_{11}$ (Fig. 6A). The contribution of $\sigma$(M–C) increases on going from Cp$_2$ZrEtCl to $\beta$-H agostic Cp$_2$ZrEt$^+$. This, together with a significant contribution from the $\sigma$(C–C$_4$) bond, results in a more strongly deshielded $\delta_{11}$ component in the latter system. In the $\alpha$-H agostic analog of Cp$_2$ZrEt$^+$ (or in Cp$_2$ZrMe$^+$), the deshielding of the $\delta_{11}$ component of the CST on the $\alpha$-carbon is significantly more pronounced. This is mostly associated with a larger contribution of the $\sigma$(M–C) orbital combined with significant contributions arising from the $\sigma$(C–C$_4$) and the $\sigma$(C–H) bonds.

Coordination of ethylene to the $\beta$-H agostic and $\alpha$-H agostic structures of Cp$_2$ZrEt$^+$ leads to distinctively different CSTs on the $\alpha$-carbon in the $\beta$-H and $\alpha$-H agostic structures of Cp$_2$ZrEt(C$_2$H$_4$)$_n$. In the case of the $\beta$-H agostic structure, the coordinated olefin leads to a significant shielding of $\delta_{11}$, mainly due to a decreased contribution of the $\sigma$(M–C) bond to deshielding. However, coordination of ethylene to the $\alpha$-H agostic analog increases the deshielding of the $\alpha$-carbon compared with $\alpha$-H agostic Cp$_2$ZrEt$^+$. This is mainly due to a strong increase of the contribution of the

Fig. 4. (A) Orientation of the CST for the $\alpha$-carbon of Cp$_2$ZrEtCl and the related $\beta$-H and $\alpha$-H (shown in gray) agostic cationic Cp$_2$ZrEt$^+$ complexes, the ethylene adducts Cp$_2$ZrEt(C$_2$H$_4$)$_2^+$, and the butyl complexes Cp$_2$ZrBu$^+$. The Gibbs energies of activation are calculated for the lowest transition state featuring the respective agostic interaction. The dashed arrows indicate that the two molecules are not directly linked by olefin insertion and that the product needs to undergo a conformational change to yield the indicated structure. (B) Orientation of the CST for systems relevant for ethylene oligomerization. The principal component values ($\delta_{iso}$) of the CSTs are given in parts per million. All Gibbs energies correspond to the reaction step as shown and are given in kilocalories mole$^{-1}$. 

A

\[ \delta_{ii} = \sigma_{\text{iso}} - \sigma_{ii} \]  
\[ \sigma = \sigma_{\text{dia}} + \sigma_{\text{para}} + \sigma_{\text{so}} \]  
\[ \langle \Psi_{\text{vac}} | \hat{I}_{\text{dia}} | \Psi_{\text{occ}} \rangle \langle \Psi_{\text{vac}} | \hat{I}_{\text{para}} | \Psi_{\text{occ}} \rangle \]  
\[ \sigma_{\text{para}} \Leftrightarrow \Delta F_{\text{vac-occ}} \]

B

Fig. 5. (A) Relevant equations (equations 1–3) and (B) pictorial representation of orbital coupling leading to deshielding.

σ(M–C) bond to deshielding (Fig. 6A). The Cp2ZrBu+ compounds behave similarly to Cp2ZrEt+.

Olefín oligomerization. The compounds related to olefin oligomerization are analyzed, focusing on Ti-based systems due to their importance in catalysis; similar patterns are obtained for the Zr and Hf analogs as reported in SI Appendix. In the Ti compounds shown in Fig. 6B, the σ(M–C) orbital constitutes the largest contribution to the δ11 component. Comparing Cp2Ti(C6H5) and Cp2Ti(C6H5) reveals that the contribution to deshielding of the σ(M–C) orbital is significantly larger in the former, in accord with the overall more deshielded δ11 component and δiso (Fig. 6B and Table 2). While the α-carbon of Cp2Ti(C6H5) is not strongly deshielded, in the cationic metallacyclopentane, Cp(η³-Ar)Ti(C6H5)+, the situation is different. This cationic metallacyclopentane shows a large deshielding on one of its α-carbons, again mostly originating from the contribution of the σ(M–C) orbital. In the cationic metallacycloheptane, Cp(η³-Ar)Ti(C6H5)+, the situation is somewhat similar, albeit that δ11 of the α-carbon is less deshielded due to a smaller contribution of the σ(M–C) orbital but also, the σ(C–C) and σ(C–H) orbitals (Fig. 6B).

Analysis of Electronic Structure Based on CSTs. Olefin polymerization. The differences in the CST values of the various compounds are mainly determined by the δ11 component, which has a similar orientation in all investigated molecules (Fig. 4). This component of the CST is hence a valuable reporter of the electronic structure of the various compounds. As noted in previous studies (57, 59–62), the large deshielding of δ11 originating from the σ(M–C) bond implies the presence of a low-lying vacant orbital oriented perpendicular to both the σ(M–C) bond and the direction of the δ11 component as illustrated in Fig. 7A. This vacant orbital originates from a p-orbital on the α-carbon, interacting with a low-lying empty metal d-orbital in the approximate σα plane that is present in all of the aforementioned systems. The interaction of the metal with the α-carbon generates a low-lying vacant orbital of π*(M–C) character, which results in the large α-carbon chemical shifts and is shown for selected compounds in Fig. 7C.

Alkylidene character and thus the presence of a π*(M–C) orbital is also evidenced in a Natural Hybrid Orbital (NHO) Directionality and Bond Bending Analysis (SI Appendix, Table S7); it is present in all systems studied in this article that are prone to undergoing ethylene insertion. The energetic capability of this orbital and hence its ability to promote the olefin insertion process are reflected in the magnitude of the deshielding. The large deshielding indicates a low energy of this orbital, since the paramagnetic term increases in magnitude with a smaller energy gap between the occupied σ(M–C) orbital and the empty π*(M–C) orbital (Fig. 5A, equation 3). The presence of this low-lying π*(M–C) orbital is associated with a low energy barrier for olefin insertion. In addition, the presence of a low-lying metal-based d-orbital induces σ(M–C) character (alkylidene character) in the M–C bond. A similar π-type overlap of an empty metal d-orbital with the α-carbon has been shown to trigger olefin metathesis activity in metallaacyclobutanes (60) and α-H abstraction in bisalkyl complexes (62).

Cp2ZrEtCl needs to lose a chloride to become an active olefin polymerization catalyst (5, 12–15, 81, 114). The calculations show that the contribution of the σ(M–C) bond to deshielding of the δ11 component increases on going from neutral Cp2ZrEtCl to cationic Cp2ZrEt+. As noted above, this trend is particularly pronounced for Cp2ZrMe+ and the α-H agostic Cp2ZrEt+, for which ethylene insertion is more favorable but less pronounced for Cp2ZrEt+ with β-H agostic interaction. Since the larger

Fig. 6. NCS analysis of the δ11 component of the CST in (A) Cp2Zr-derived compounds related to olefin polymerization and (B) Cp2Ti- and Cp(η³-Ar)Ti+-derived compounds related to olefin oligomerization.
that the agostic creased increase in alkylidene character favors insertion. In fact, the in- 
tronic structures, with the latter showing a much larger the ethylene insertion process, which is significantly higher in the 
orbital, which ultimately leads to forming and breaking of 
In-phase mixing of the A 
reactive toward olefin insertion.

do x is that the shorter 
α-H agostic structure, while the insertion is virtually barrierless in 
A-H agostic structure, respectively). The apparent para-
dox is that the shorter α-H agostic M–C bond is found to be more reactive toward olefin insertion.

The Cp₂ZrBu⁺ species generated on insertion displays a CST for the α-carbon similar to Cp₂ZrEt⁺ for both the β-H-agostic and the α-H-agostic forms, indicating that the foregoing analysis also applies to the subsequent ethylene insertions during polymer-chain growth.

Olefin oligomerization. We performed a similar analysis on the ethylene complex Cp₂Ti(C₂H₄). In free ethylene, the deshielding mostly arises from the magnetically induced coupling of the σ(C–C) orbital to the vacant π*(C–C) orbital (Figs. 5A, equation 3 and 8A). In the ethylene complex Cp₂Ti(C₂H₄), the largest part of the deshielding arises from a coupling of the occupied σ(M–C) orbital with the vacant π*(M–C) orbital (Fig. 8B). This situation resembles what is observed in the cationic metal-alkyl complexes (e.g., Cp₂M–R⁺) (Fig. 7A), and it is a signature of the reactivity of the M–C bond toward olefin insertion and hence, ring expansion to yield a metallacycloptene.

In the corresponding metallacycloptene Cp₂Ti(C₂H₄), the α-carbons are significantly less deshielded, mainly due to a smaller deshielding of the δ₁₁ components. According to the NCS analysis, this is caused by a significantly decreased contribution of the σ(M–C) bond to δ₁₁ (Fig. 6B). This indicates that the M–C bonds of Cp₂Ti(C₂H₄) contain less π-(alkylidene) character. In sharp contrast, the cationic analog Cp(η⁵-Ar)Ti(C₂H₄)⁺ retains a large deshielding on one of the α-carbons (δₖ = 122 ppm and δ₁₁ = 235 ppm). Again, the largest contribution to δ₁₁ arises from the σ(M–C) bond, indicating that Cp(η⁵-Ar)Ti(C₂H₄)⁺ retains a significant alkylidene character, and is thus prone to further ethylene insertion (Fig. 6B). The resulting metal-
acycloptene Cp(η⁵-Ar)Ti(C₂H₄)⁺ shows slightly less deshielding (δₖ = 115 ppm and δ₁₁ = 200 ppm). This observation correlates with the Gibbs energies of activation (and cor-
responding reaction free energies) for the metallacycloptene formation from Cp₂Ti(C₂H₄) and Cp(η⁵-Ar)Ti(C₂H₄), which are found to be at 51.0 kcal mol⁻¹ (−4.1 kcal mol⁻¹) and 15.5 kcal mol⁻¹ (−25.4 kcal mol⁻¹), respectively (Fig. 4B shows the Gibbs energy profile). Also, in these systems related to ethylene oligomeri-
zation, the NHO Directionality and Bond Bending Analysis indicates the presence of α-character in the M–C bonds that are prone to insert olefins and feature a deshielded α-carbon (SI Appendix, Table S7).

Discussion

All calculations and experimental evidence from the literature agree that insertion of ethylene into a metal–carbon bond of a low-electron count transition metal, such as a cationic species like Cp₂Ti–CH₂R⁺, is an exoergic reaction that proceeds with a small Gibbs activation energy. The net reaction is classified as a [2r + 2x] cycloaddition, which would be symmetry forbidden in organic transformations but can occur in the presence of transition metals. It is thought that the activation energy is influ-
cenced by a distortion of [M]–CH₂R in the ground and/or the transition state, resulting in a short M...Hₓ contact distance in the structure of the catalyst (26). The resulting shortened metal–
carbon bond distance is often associated with an acute [M–C–H] angle and an increase in the C–H distance; this distortion is

Fig. 7. (A) Magnetically induced orbital couplings that give rise to deshielding of the α-carbon. (B) Orbital interaction of the M–C bond with the olefin π*(C–C) orbital, lowering the energy of π(M–C). (C) Calculated and schematic vacant orbitals of π*(M–C) character constructed from a vacant metal d-orbital and contributions from the α-carbons.
referred to as an α-H agostic interaction. The α-H agostic interaction is attributed in part to the donation of electron density from the α-C–H bond to a vacant metal orbital (21, 115–117), resulting in a lowering of the \( J_{\text{C-H}} \) coupling constant due to the increased p character in the C\(_{\text{α-H}}\) bond.

In this article, the measured solid-state NMR tensors show that the α-carbon is highly anisotropic, unexpected for an α-alkyl. Computations indicate the specific orientation of the anisotropic CST, with the most deshielded component (\( \delta_{\text{iso}} \)) oriented perpendicular to the horizontal symmetry or pseudosymmetry plane of the molecules (Fig. 4). NCS analysis shows that the deshielding originates from the presence of a low-lying empty metal d-orbital that interacts in a π-fashion with a filled carbon p-orbital, perpendicular to the M–C bond that is also involved in the C–H bond. Therefore, the α-C–H interaction, referred to as an agostic C–H bond, is a manifestation of the π-donation of the alkyl ligand to the electron-deficient metal center. This gives some alkylidene character to the single M–C bond and results in a shortening of the M–C distance as proposed in one of the initial discussions of the α-C–H agostic interaction (115). A corollary is that the alkylidene character is responsible for the geometric distortion observed in an α-C–H agostic interaction.

The CST hence probes the frontier molecular orbitals that participate in the insertion step, thus correlating chemical shift, in particular \( \delta_{\text{iso}} \), to reactivity. Olefin insertion is favored for metal-alkyl compounds with alkylidene character, reminiscent of the reaction of an olefin with metal alkylidenes in the olefin metathesis reaction (Fig. 9). In this analogy, the difference between olefin metathesis and olefin insertion is only in the degree of alkylidene character in the M–C bond, since in both cases, an olefin reacts with a metal–carbon bond bearing a π-character. In the case of olefin metathesis, there is a formal \( \pi(M=C) \) bond in the alkylidene that enables the formation of a metalacyclobutane intermediate in the \([2+2]\) cycloaddition reaction. In an olefin insertion process, the M–C bond only carries partial π-character, resulting in the formation of a homologous metal-alkyl product rather than a metalacyclobutane product. The foregoing analogy shows the complementarity between the Cossee–Arlman and the Green–Rooney mechanisms (Fig. 1); the Cossee–Arlman mechanism suggests that the olefin insertion takes place at a metal-alkyl complex with a vacant coordination site, while in the Green–Rooney mechanism, the olefin is activated by the metal alkylidene. Hence, the difference between the Cossee–Arlman and the Green–Rooney mechanisms is merely in the extent of \( \pi(M-C) \) character in the M–C bond.

Based on the foregoing analysis, the role of charge in olefin insertion is delineated, since a positive charge on the metal-alkyl compound lowers the energy of the d-orbitals, bringing them closer in energy to the filled ligand orbitals and allowing for a stronger \( \pi(M-C) \) bonding interaction and the lower activation energies for olefin insertion.

Similarly, the observed CSTs account for the reactivity of (Bu\(_2\))\(_3\)Ti systems (studied in the isoglobal Cp\(_2\)M compounds) toward ethylene. The ethylene adduct Cp\(_2\)Ti(C\(_2\)H\(_4\)) shows significant alkylidene character and is prone to insert an additional molecule of ethylene. However, the M–C bond of the resulting metallacyclopentane does not show significant alkylidene character; accordingly, it is not reactive toward olefin insertion and does not undergo further ring expansion. Instead, rather stable metallacyclopentanes or β-H abstraction processes are observed, generating 1-butene. In contrast, the metallacyclopentane in the cationic Cp(\( \eta^3\)-Ar)Ti\(^+\) system retains a significant alkylidene character on one α-carbon as evidenced by a large deshielding. This also accounts for the shorter calculated M–C bond distance (2.025 Å in Cp(\( \eta^3\)-Ar)Ti(C\(_2\)H\(_4\))\(^+\) vs. 2.164 Å in Cp\(_2\)Ti(C\(_2\)H\(_4\))). Hence, for the cationic species, further reactivity toward ethylene insertion is expected and observed. In the resulting metalacycloheptane, the α-carbon is slightly less deshielded (\( \delta_{\text{iso}} \) decreases by 35 ppm, the contribution of n(M–C) by 11 ppm). This indicates a slightly decreased alkylidene character of the M–C bond, consistent with the slightly higher transition-state energy for ethylene insertion into Cp(\( \eta^3\)-Ar)Ti(C\(_2\)H\(_4\))\(^+\) vs. Cp(\( \eta^3\)-Ar)Ti(C\(_2\)H\(_4\))\(^+\) (17.2 vs. 15.5 kcal mol\(^{-1}\)). Combined with the rather low free energy of activation (14.0 kcal mol\(^{-1}\)) for β-H abstraction at the metalacyclopentane Cp(\( \eta^3\)-Ar)Ti(C\(_2\)H\(_4\))\(^+\), this explains the preferred formation of 1-hexene over further ring expansion and formation of 1-octene and higher oligomers.

The analysis of the α-carbon CST values reveals some striking but informative differences between β-H and α-H agostic interactions. Agostic interactions are traditionally described as three-center, two-electron interactions between a C–H bond and a metal site (7, 8, 21, 117). Hence, in these structures, the C–H bond is a two-electron ligand interacting with the metal. This view is in line with the CST analysis for the β-H agostic structures. The β-C–H bond interacts with a low-lying metal orbital, thus raising this orbital’s energy and decreasing its ability to develop a π-interaction with the α-carbon (hence the more shielded α-carbon chemical shift and lower reactivity). In an α-H agostic structure, the situation is markedly different. The small M–C\(_{\alpha-H}\) angle is a reporter of a p-orbital on the α-carbon interacting with a low-lying metal d-orbital. Hence, this type of

![Fig. 9. Parallels between (A) olefin metathesis and (B) olefin insertion.](image-url)
structure evidences alkylidine character in the M–C bond associated with higher reactivity. While the β-H agostic interaction leads to a stabilization of a metal-alkyl species and disfavors olefin insertion, the α-H agostic interaction provides π-character to the M–C bond and makes it reactive toward olefin insertion. β-H and α-H interactions are phenomenologically similar, but they have a fundamentally different origin.

Epilogue. The detailed analysis of chemical shifts by determining CSTs using solid-state NMR augmented with computational analysis defines the nature of the frontier molecular orbitals. Since frontier molecular orbitals are the active orbitals that are involved in making and breaking chemical bonds, the anisotropy of the NMR chemical shifts of carbon nuclei (bound to a metal) maps their electronic and structural changes along the reaction coordinate. This article focuses on a selected subset of catalysts used in olefin oligo- and polymerization processes and connects them with the olefin metathesis catalysts by sharing a similar [2 + 2]-cycloaddition step, specifically coined as insertion, that is forbidden in the absence of catalysts. The catalysts for these related processes—oligomerization, polymerization, and metathesis—all fulfill the same condition: they have two low-lying empty orbitals at the metal of appropriate topology to engage in the reaction: one to coordinate the olefin and one to install a π-character in the metal–carbon bond to facilitate olefin insertion. Fig. 10 highlights the similarity of the topology between metal-alkylidene and -alkyl compounds, which differ merely in the degree but not in the nature of π-bonding. Hence, while olefin metathesis proceeds via a formal [2 + 2] cycloaddition, olefin insertion can be considered in a similar manner, since the two reactions are isobolal (60). It, therefore, follows not surprisingly that d⁰ Cp²M fragments are common to both polymerization and olefin metathesis catalysts and that d⁰ X₂M(=NR) fragments are found in oligomerization and metathesis catalysts.

The ¹³C NMR chemical shift and most notably δ₁₁ are directly linked to the low activation barrier of olefin insertion, since both result from the same low-lying empty orbital of π*(M–C) character. Accordingly, it is a descriptor that predicts the reactivity of d⁰ transition-metal-alkyl compounds in olefin oligomerization and polymerization processes. While it does not allow for discriminating highly efficient from average catalysts due to the complexity of catalytic processes, chemical shift and more precisely the CST provides a descriptor and thereby a guideline to design potentially efficient catalysts.

Materials and Methods

All measured samples were prepared according to procedures reported in the literature or modifications thereof, and their NMR spectra were recorded in 1D or 2D cross-polarization magic angle spinning experiments to extract the principal components of the CST (SI Appendix, Experimental Section). Molecular structures were optimized with the hybrid Perdew-Burke-Ernzerhof functional using quasi-relativistic effective core potentials from the Stuttgart group, the associated basis sets on metal atoms, and a triple-ζ pseu-2 basis set on all other atoms. NMR parameters were calculated using DFT/ZORA calculations. The calculated shielding tensors were analyzed using scalar-relativistic natural localized molecular orbitals. Energies were calculated as single-point calculations from optimized structures, including the effects of dispersion ( Grimme dispersion model GD3) and solvent (solvent model based on density, toluene) (SI Appendix, Computational Details).

ACKNOWLEDGMENTS. C.P.G. is supported by the Swiss National Science Foundation Grant 200020_149704 and is a recipient of the Scholarship Fund of the Swiss Chemical Industry. S.S. thanks the Osaka University Scholarship for Overseas Research Activities 2017. K.Y. thanks the Canon Foundation for a postdoctoral fellowship. O.E. was partially supported by the Research Council of Norway through its Centres of Excellence Scheme Project 262695. O.E. and C.C. thank the Miller Fellowship Program at University of California, Berkeley, which has fostered the discussions from which this work emanates.


