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Influence of the 4-Substituents on the Reversal of Enantioselectivity in the Asymmetric Hydroformylation of 4-Substituted Styrenes with $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP]

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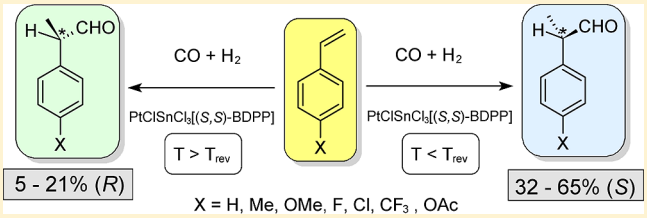
Supporting Information

ABSTRACT: The enantioselectivity of the asymmetric hydroformylation of 4-substituted styrenes in the presence of an in situ catalyst, formed from $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP] and tin(II) chloride, was influenced by the reaction temperature. The preferred formation of the *S* and the *R* enantiomers of the branched aldehyde regioisomers (**2a**−**g**) was observed at low and high temperatures, respectively. The electron-donor or electron-acceptor properties of the para substituents of styrene show correlation with the changes in enantioselectivity, especially with the reversal temperature of the enantioselectivity. The reversibility of the formation of the Pt-branched alkyl intermediates, leading to the corresponding *R* and *S* enantiomers of 2-arylpropanals, depends on the Hammett constants. The electronic effect of para substituents was investigated by quantum chemical methods employing the simple olefin adducts $[HPt(PH_3)_2(olefin)(SnCl_3)]$. Excellent linear correlation was found between the para substituent constants and the electrostatic potential at nuclei of the platinum atom. Equally good correlation has been established for the other atoms as well in the coordination sphere of Pt.



INTRODUCTION

The importance of the highly selective hydroformylation of alkenes has mainly been shown in two fully different fields: (i) the regioselective hydroformylation of propene to give the linear aldehyde regioisomer *n*-butyraldehyde, in the presence of cobalt- and rhodium-containing catalysts, has successful industrial-scale application and has seen detailed mechanistic investigations[1,2] and (ii) the enantioselective hydroformylation of vinyl aromatics to 2-arylpropanals in the presence of rhodium and platinum catalysts has potential applications in the synthesis of nonsteroidal anti-inflammatory drugs, such as ibuprofen, naproxen, and suprofen.[3,4]

As for the platinum-catalyzed hydroformylation, soon after the discovery of the hydroformylation activity of platinum−monophosphine−tin(II) halide type in situ systems,[5] the corresponding "preformed" $PtCl(SnCl_3)$(chiral diphosphine) catalysts and $PtCl_2$(chiral diphosphine) + tin(II) halide in situ systems were used in enantioselective hydroformylation.[6] Even the first publications have shown the efficiency of these systems both in the synthesis of chiral 2-arylpropanal derivatives and in that of the chiral building blocks obtained in the highly enantio- and regioselective hydroformylation of 1,1-disubstituted olefins.[7] To increase enantioselectivities and catalytic activities in platinum-based hydroformylation, widespread investigations were carried out using various types of chiral mono- and bidentate phosphorus ligands.[8] On the other hand, the applicability of tin(II) halide free hydroformylation catalysts such as diphenylphosphinous acid platinum complexes[9] or in situ systems formed from platinum−alkyl/aryl complexes and boron additives was shown.[10]

While great efforts have been made in finding the optimum performance of the catalysts in terms of activity and chemo-, regio-, and enantioselectivity, fewer results have been published on the better understanding of the fine mechanistic details. The elementary steps of the generally accepted mechanism such as alkene coordination and its insertion into the Pt−H bond, carbon monoxide coordination and its insertion into the Pt−alkyl bond, and the formation of the aldehyde in the hydrogenolysis of the Pt−acyl complex have been investigated by both analytical[11] and computational[12] means. (It is worth noting that a number of similar studies have been published on the mechanism of rhodium-catalyzed hydroformylation.[13,14]) The importance of the good leaving properties of the trichlorostannato ligand forming cationic intermediates with trichlorostannate counterion was also shown by high-pressure NMR studies.[15]

Regarding the fundamental understanding of the enantioselectivity in hydroformylation, and especially the exciting phenomenon of the reversal of enantioselectivity in the hydroformylation of styrene[8d,e] in the presence of $PtCl(SnCl_3)$-[(2*S*,4*S*)-BDPP)] precursor, a seminal work was published by Casey et al.[16] Their investigations on the platinum-catalyzed deuterioformylation of styrene established that the platinum hydride addition to styrene, i.e., styrene insertion into the Pt−

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H bond forming a Pt−alkyl intermediate, is largely irreversible at low temperature (40 °C) but reversible at higher temperature (100 °C).

Landis and co-workers reported the Rh-catalyzed hydroformylation of terminal and internal aryl alkenes employing diazaphopholane ligands. 4-Substituted styrenes provided high regio- and enantioselectivities. Interestingly, in the presence of (*S*,*S*,*S*)-BisDiazaphos ligand the Hammett constant of the para substituents showed a linear correlation with the logarithm of the branched/linear ratio of the aldehydes. Both the regioisomer and enantiomer ratios were found to be proportional with the carbon monoxide partial pressure but approximately independent of the H_2 pressure. Deuterioformylation studies revealed that the pressure effect arises from the kinetic competition between the reaction of the branched alkyl rhodium complex with CO, resulting in the corresponding acyl complex, and the reversion of the alkyl species to Rh hydride and olefin by β-elimination.[17]

This paper describes the asymmetric hydroformylation of seven 4-substituted styrenes in the presence of an in situ catalyst formed from $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP] and tin(II) chloride. Here we report on the influence of the electron-donor or electron-acceptor properties of the para substituents of styrene, which show characteristic changes in the enantioselectivity and, especially, in the temperature of the reversal of the enantioselectivity. The second goal of this study is to establish a clear correlation between the electronic effects of the para substituents and the Hammett substituent constant by means of a selected quantum chemical descriptor, namely the electrostatic potential at nuclei for all atoms in the coordination sphere of platinum, including the Pt center itself.

EXPERIMENTAL SECTION

General Considerations. The $PtCl_2(PhCN)_2$ precursor was synthesized from $PtCl_2$ (Aldrich) according to a standard procedure.[18] The $PtCl_2$[(2*S*,4*S*)-BDPP] and $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP] precursors were synthesized as described in one of our earlier papers.[8d,e] Toluene was distilled and purified by standard methods and stored under argon. 4-Substituted styrenes and tin(II) chloride (anhydrous) were used as obtained from Sigma-Aldrich without any further purification. All reactions were carried out under an argon atmosphere using standard Schlenk techniques.

Mass spectrometry data have been obtained using a GC-MS system consisting of a Perkin-Elmer AutoSystem XL gas chromatograph. The GC and chiral GC measurements were run on a Chrom-Card Trace GC-Focus GC gas chromatograph. The enantiomeric excesses were determined on a capillary Cyclodex column; (*S*)-2-arylpropanals eluted before the *R* enantiomers.

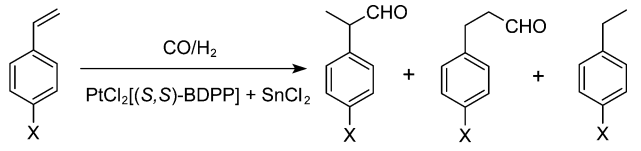
Hydroformylation Experiments. In a typical experiment, a solution of $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP] (9.0 mg; 0.01 mmol) and tin(II) chloride (1.9 mg; 0.01 mmol) in toluene (10 mL) containing styrene derivatives (**1a−g**; 2.0 mmol) was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was pressurized to 80 bar total pressure (CO/H_2 = 1/1) and placed in an oil bath of constant temperature. The mixture was stirred with a magnetic stirrer for the given reaction time. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC-MS and chiral GC.

Computational Details. For all of the calculations the PBEPBE gradient-corrected functional by Perdew, Burke, and Ernzerhof[19] was selected using the Gaussian 09 suite of programs.[20] For platinum and tin the Stuttgart/Dresden basis set (denoted as SDD) was used, which is triple-ζ for platinum and double-ζ for tin with contraction patterns of (8s,7p,6d) → (6s,5p,3d) and (4s,4p) → (2s,2p), treating 60 and 46 electrons as core electrons, respectively.[21] For all other atoms the 6-31G(d,p) basis set[22] was employed. Optimized structures were identified by the absence of the negative eigenvalues. The electrostatic potential values were directly obtained from the Gaussian 09 output of the MESP calculations. Charge decomposition analysis (CDA) calculations[23] have been performed utilizing the AOMix software.[24]

RESULTS

To determine whether the substituents of styrene have any influence on the enantioselectivity and the temperature dependence of enantioselectivity, hydroformylation experiments of various 4-substituted styrenes (**1a−g**) catalyzed by an in situ system, formed from $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP] and tin(II) chloride, were conducted at various temperatures with 80 bar of a CO/H_2 (1/1) mixture (Scheme 1). It is worth noting that some catalytic activities were observed even at room temperature; however, the evaluation of the catalysts was carried out in the temperature range 40−120 °C.

Scheme 1. Hydroformylation of 4-Substituted Styrenes in the Presence of $PtCl(SnCl_3)$[(2*S*,4*S*)-BDPP] + $SnCl_2$ Catalyst



a X=H
b X=CF_3
c X=Cl
d X=F
e X=CH_3
f X=OCH_3
g X=OAc

Regarding chemoselectivity toward aldehydes, two features have to be emphasized. (i) The tendency of decreasing chemoselectivity toward aldehydes with increasing reaction temperature was observed with all substrates **1a−g**. For example, 92, 90, 86, 80, and 73% chemoselectivities were obtained using **1b** as substrate at 40, 60, 80, 100, and 120 °C, respectively (Figure 1).

(ii) On comparison of chemoselectivities obtained with various substrates at the same temperature, small differences have only been observed at low reaction temperatures, while a wider range of chemoselectivity was obtained at higher temperatures. For example, the chemoselectivities obtained for **1a−g** at 60 and 100 °C were varied in the ranges of 89% (**1g**) to 94% (**1f**) and of 79% (**1g**) to 88% (**1f**), respectively (Figure 1).

The regioselectivity toward branched aldehydes (**2a−g**) show a characteristic decrease by increasing temperature. While the two aldehyde regioisomers were formed in nearly equimolar amounts at 40 °C with all substrates, the highly preferred formation of the linear aldehydes (**3a−g**) was observed at 100 °C. An especially low preference for the branched aldehyde regioisomers was shown with **1b−d**, containing the electron-acceptor substituents 4-trifluoromethyl, 4-chloro, and 4-fluoro, respectively (Figure 2).

The diagram of ee vs reaction temperature, obtained in the asymmetric hydroformylation of 4-substituted styrenes **1a−g** (Figure 3), reflects the same phenomenon as observed

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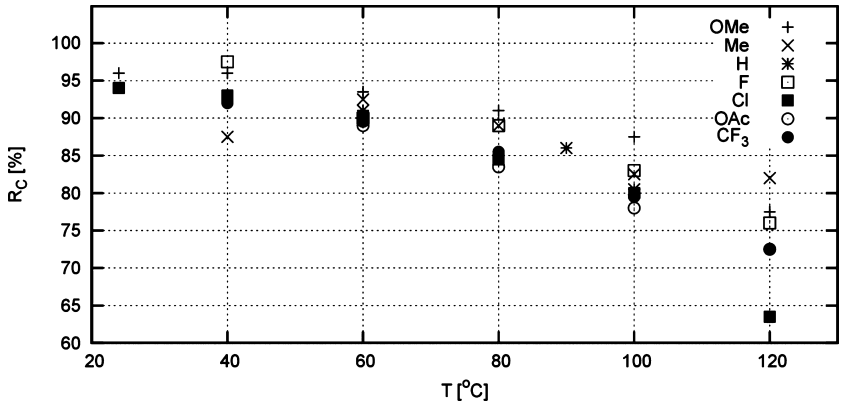

Figure 1. Effect of temperature on the chemoselectivity toward aldehydes in the hydroformylation of **1a**−**g**.

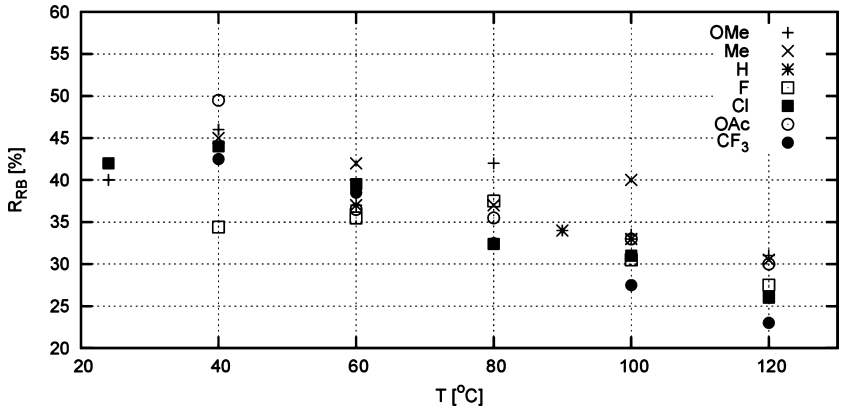

Figure 2. Effect of temperature on the regioselectivity toward branched aldehyde in the hydroformylation of **1a**−**g**.

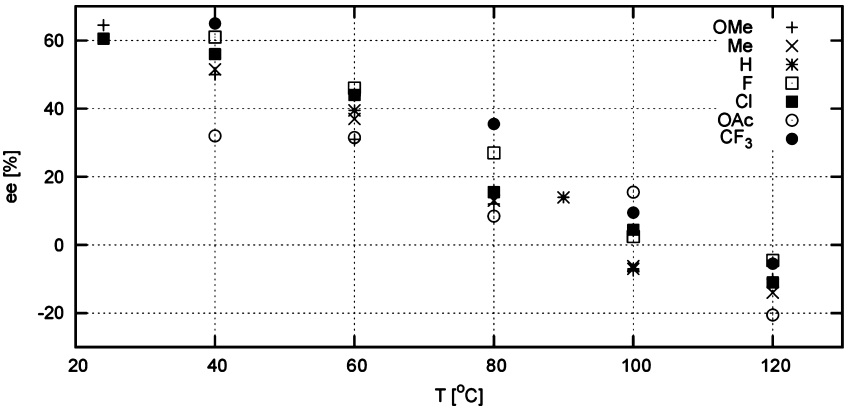

Figure 3. Effect of temperature on enantioselectivity in the hydroformylation of **1a**−**g**.

previously with styrene (**1a**) in the presence of Pt-BDPP-tin(II) halide[8d,e,n] and Pt-BDPP-4-NMe_2-tin(II) halide[8m] in situ catalysts or in the presence of the corresponding $PtCl(SnCl_3)$-(BDPP) precursor.

That is, the formation of the (*S*)-2-arylpropanals **2a**−**g** is favored at low temperatures, while the *R* enantiomers predominate at higher temperatures also in the present investigation. When the temperature of the reversal of the enantioselectivity, i.e., the temperature of the change of the absolute configuration of the dominating enantiomer, is plotted against Hammett constants (σ_{para}) (Figure 4), a correlation was observed. It was found that the substituents with electron-acceptor properties increase the reversal temperature. The reversal of enantioselectivity occurred at 102, 105, and 107 °C with fluoro (σ_{para} = +0.062), chloro (σ_{para} = +0.227), and trifluoromethyl (σ_{para} = +0.540) substituents, respectively. Accordingly, a decrease of the reversal temperature was observed with electron-donor substituents. That is, the reversal of the enantioselectivity occurred at 95 and 92 °C with methyl (σ_{para} = −0.170) and methoxy (σ_{para} = −0.268) substituents, respectively. The only exception that does not fit into this tendency is the acetoxy substituent (σ_{para} = +0.310), with a reversal temperature of 87 °C. Its Hammett constant would predict an increased reversal temperature (above 100 °C), close to that of the chloro substituent. In contrast to data published earlier,[23] the above catalytic investigations predict a much more negative Hammett parameter for *p*-acetoxy substituents. The re-evaluation of σ_p for the OAc group has been completed by

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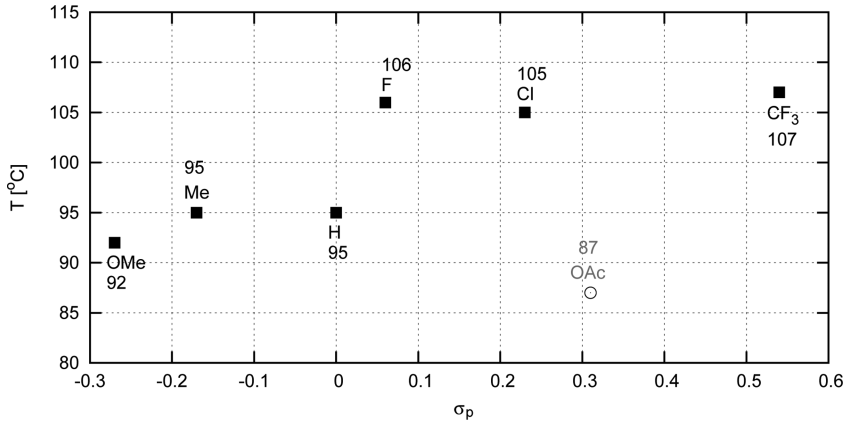


Figure 4. Reversal temperatures of the enantioselectivity plotted against the Hammett constants.

employing quantum chemical descriptors as well as by computing the relative acidity of substituted benzoic acids in the water phase.[26] As a result of both approaches a new value of −0.02 has been suggested, urging the revision of the old Hammett parameter known from the literature.

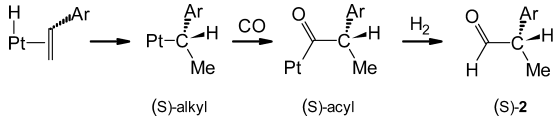
It is worth noting that the temperature of the reversal of enantioselectivity, i.e., the reaction temperature resulting in racemic mixtures, was determined experimentally as accurately as possible for **1a**−**g**. Therefore, hydroformylation reactions were carried out at intermediate temperatures in this range. For instance, the catalytic experiments were conducted at 92 and 87 °C in the case of **1f** (ee 1% (*R*)) and in the case of **1g** (ee 1% (*R*)), respectively.

DISCUSSION

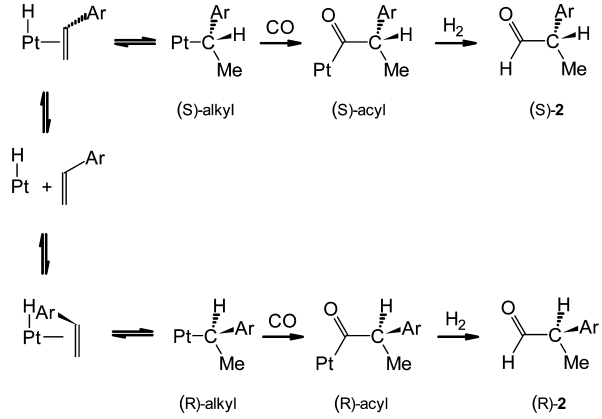
We focused our attention on the stereodefining step of the enantioselective hydroformylation with Pt-BDPP systems, that is, on the stage, where the stereochemical outcome of the asymmetric hydroformylation is determined. We aimed at explaining the characteristic influence of the 4-substituent of styrene on the reversal of the enantioselectivity as a function of reaction temperature. In accordance with previous findings, the preferred formation of (*S*)-2-arylpropanals have been observed at low temperature, while the *R* enantiomers predominate at higher temperature when the hydroformylation of the corresponding 4-substituted styrene **1a**−**f** was carried out in the presence of Pt-(2*S*,4*S*)-BDPP-tin(II) chloride catalytic systems.

The detailed deuterioformylation experiments of Casey et al. revealed that the formation of the Pt-alkyl intermediate is largely irreversible at low temperature: i.e., *β*-hydride elimination is not favored (Scheme 2). Therefore, the predominating enantiomer (*S*)-**2** using (2*S*,4*S*)-BDPP) is determined by the difference in the relative rates of the formation of the Pt-(*S*)-alkyl and Pt-(*R*)-alkyl intermediates. The olefin insertion as an enantioselectivity-determining step was also corroborated by computational studies, modeling Pt-catalyzed hydroformylation containing the (2*S*,3*S*)-chiraphos) ligand, which forms a more rigid chelating ring with platinum in comparison to BDPP.[27] However, the reversibility of the same step was observed by Casey at higher temperature, resulting in free styrene which is prone to insert into the platinum−hydride bond to provide the opposite alkyl enantiomer (Scheme 3).

Scheme 2. Formation of the (*S*)-2 Branched Formyl Regioisomers at Low Temperature



Scheme 3. Formation of the (*R*)-2 Branched Formyl Regioisomers at High Temperature



One of the key points of these investigations is the determination of the relative rates of hydrogenolysis (product-forming step): the hydrogenolysis of the Pt-(*S*)-acyl enantiomer is slower than that of the corresponding Pt-(*R*)-acyl species by a factor of about 6 using Pt-(2*S*,4*S*)-BDPP catalyst.[16]

Our results have shown that the reversal of the enantioselectivity occurs in the temperature range 87−107 °C depending on the electron-donor/electron-acceptor properties of the 4-substituents of the substrate. Keeping in mind the above steps which determine the formation of (*S*)- and (*R*)-**2a**−**g**, it could be stated that the electron-acceptor substituents decrease the reversibility of the Pt-alkyl-forming step as a function of temperature. Since the reversal temperature in the hydroformylation of **1b** is increased relative to that of styrene (**1a**), a facile insertion of carbon monoxide but not a *β*-hydride elimination resulting instyrene can be supposed.

According to the present studies, the electron-donor substituents increase the reversibility of Pt-alkyl formation; i.e., they decrease the reversal temperature of enantioselectivity. These substituents, such as CH_3 and OCH_3, increase electron

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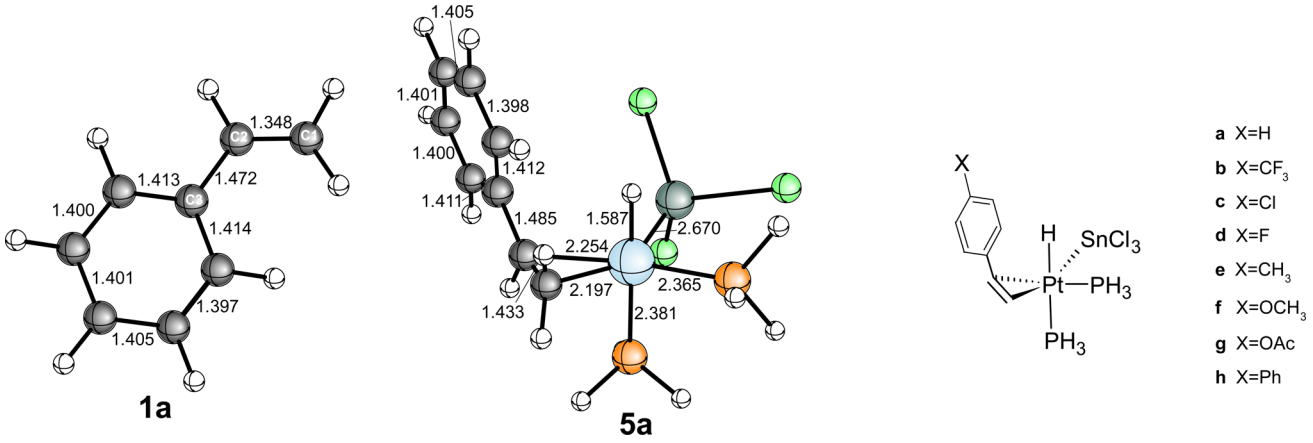

Figure 5. Computed structures of uncoordinated styrene (**1a**) and model compound $HPt(PH_3)_2(SnCl_3)$(styrene) (**5a**).

density on the Pt−carbon bond of the (*S*)-alkyl intermediate. In contrast to the above cases involving electron-acceptor substituents, *β*-hydride elimination is preferred to carbon monoxide insertion, resulting in the "re-formed" styrenes **1e**,**f**, respectively. Their insertion into the Pt−H bond leads to the favored formation of the corresponding *R* enantiomers (*R*)-**2e** and (*R*)-**2f**, respectively.

COMPUTATIONAL STUDIES

In order to elucidate the effect of the para substituent on styrene, the simple model compounds $HPt(PH_3)_2(SnCl_3)$(4-substituted styrene) (see Figure 5), denoted as **5a**−**h**, have been selected, providing a straightforward description for Pt-phosphine-$SnCl_2$ systems containing a coordinated styrene. In comparison to experiments, the set of substituents has been extended with the uncoordinated and coordinated 4-phenylstyrene, which are denoted as **1h** and **5h**, respectively. The metal-hydrido-olefin adduct is usually high in terms of free energy, but it is not available as a separate complex to study spectroscopically, although it plays a vital role in the key step of olefin activation.

The molecular electrostatic potential (MESP) is a function of the electron density. The three-dimensional MESP is a fundamental quantity, extensively applied for chemical and biological reactivity.[28] The MESP, for instance, in the form of an isosurface, can delineate negative regions in a molecule which are subject to electrophilic attack. Lone pair regions in P-donor ligands, for example, reveal negative MESP in the lone pair region and can readily be characterized by the minimum of the most negatively valued point (V_{min}).[29] For the coordinating power of NHC ligands the MESP at the carbene carbon revealed even better correlation with Tolman electronic parameters in comparison to V_{min}.[30] For quantum chemical descriptors in the present study the electrostatic potential at nuclei (EPN) has been chosen, which is a very frequently used electronic property in chemistry for describing substituent effects. The EPN can be calculated using eq 1, where Z_A is the

$$V_Y \equiv V(R_Y) = \sum_{A \neq Y} \frac{Z_A}{|R_Y - R_A|} - \int \frac{\rho(r')}{|R_Y - r'|}\, dr' \qquad (1)$$

nuclear charge of atom A with radius vector R_A and $\rho(r')$ is the electron density of the molecule. It was found recently that the EPN of the acidic hydrogen of substituted benzoic acid showed excellent linear correlation with the para Hammett constants.[26]

The C1−C2 bond undergoes substantial elongation upon coordination to the platinum center. The change in bond strength is also reflected in the C1−C2 Wiberg bond indexes (WBIs), which are 1.885 and 1.358 for **1a**, and **5a**, respectively. The WBI for C2−C3 is also decreased from 1.105 to 1.082 when styrene is coordinated to the Pt center.

The Hammett para substituent constants for **1a**−**h**, as well as those for complexes **5a**−**h**, are depicted in Figure 6 in the function of the EPN of the terminal vinylic carbon (C1). Excellent linear correlation has been obtained in both cases with σ_p; somewhat better for substituted styrenes (r^2 = 0.978) than for their corresponding olefin complexes (r^2 = 0.961). As expected, the EPN drops off upon coordination to platinum, in line with the decrease of electron density around the terminal carbon due to the electron donation to the $HPt(PH_3)_2(SnCl_3)$ moiety.

The C2 atom of the vinyl group shows a very similar behavior with a somewhat smaller, yet still satisfactory linear correlation (r^2 = 0.932) (see Figure S1 in the Supporting Information). Better linear correlation (r^2 = 0.967) have been achieved between the EPN of platinum and σ_p (see Figure S2 in the Supporting Information). The good linear correlation remains between σ_p and the phosphorus atoms as well, as the r^2 values are 0.958 and 0.961 for the P atom of the axial and equatorial PH_3 ligands, respectively. The equatorial phosphorus is more negative in comparison to the axial phosphorus, which may be attributed to the donating effect of the in-plane vinyl group, resulting in a slightly greater increase in electron density of the coordinating atoms belonging to the equatorial ligands (Figure S3 in the Supporting Information). Similarly, the EPN of the hydrido ligand also correlates well with σ_p of the para substituent (r^2 = 0.949; Figure S4 in the Supporting Information). Surprisingly, the best linear correlation has been achieved for the tin atom of $SnCl_3$, with r^2 = 0.972. Figure 7 depicts the relationship between the EPN of tin and σ_p of the para substituents of styrenes.

Thus, the para substituent of styrene has an effect not only on the electron density of the coordinating vinyl group but also on the platinum center as well as on the other atoms in the coordination sphere of Pt. The effect of σ_p on the electrostatic potential in the nucleus of Sn (V_{Sn}) is depicted in Figure 7. The linear correlation between the σ_p and all atoms in the platinum-hydrido-olefin complex, which may play a crucial role

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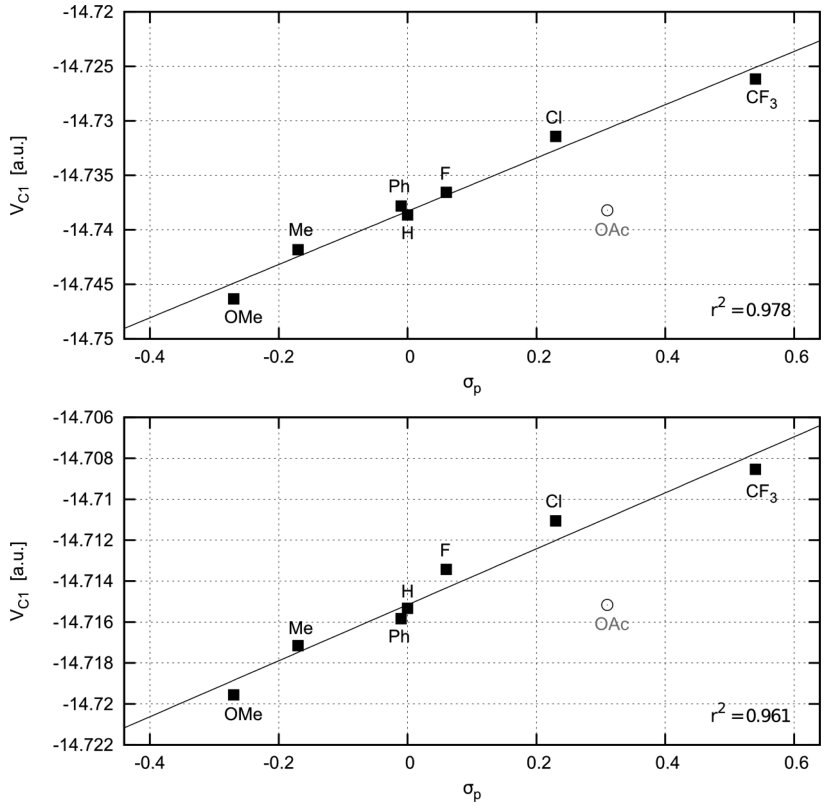

Figure 6. Relationship between the Hammett para substituent constants and the electrostatic potential in the nucleus of the terminal carbon atom of uncoordinated 4-substituted styrenes (top) and of those in the corresponding complexes $[HPt(PH_3)_2(4\text{-substituted styrene})(SnCl_3)]$ (bottom).

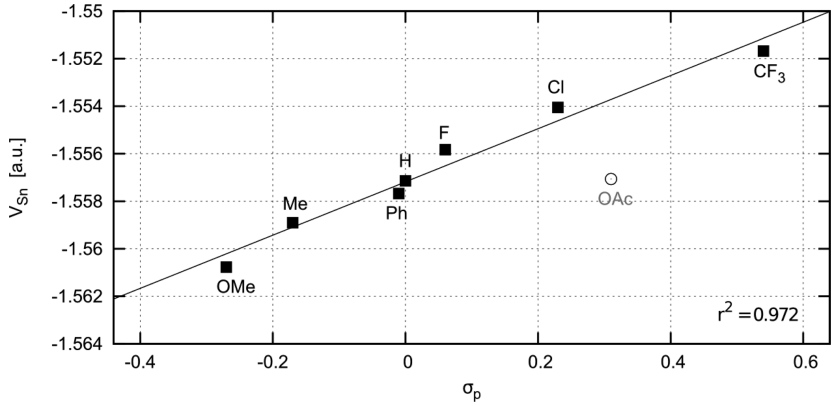

Figure 7. Relationship between the Hammett para substituent constants and the electrostatic potential in the nucleus of tin in the complexes $[HPt(PH_3)_2(olefin)(SnCl_3)]$.

influencing the outcome in every elementary step in Pt-catalyzed hydroformylation, may provide an explanation why measurable quantities of the catalytic reaction, such as the enantioselectivity, show correlation with the σ_p of the substituent on styrene. In accord with our recent studies[26] on para-substituted benzoic acids and substituted benzenes the computed σ_p of the OAc group reveals a remarkable difference from the value known from the literature (+0.31).[25]

It should be noted that the reason for the use of PH_3 as ligand was to eliminate the steric and other effects of the phosphine, since in our case only the electronic influence of the 4-substituted styrene was in question. Nonetheless, the calculations were repeated for the *cis*-$[HPt(PPh_3)_2(SnCl_3)$(4-substituted styrene) complexes as well, in order to inspect the effect of triphenylphosphine (see Figures S5−S7 in the Supporting Information). Again, for Pt and Sn good linear correlation was obtained with σ_p (0.972, and 0.916, respectively); however, much worse correlation was found for the hydride ligand (0.569), which might be attributed to the combined steric and electronic effects of the triphenylphosphine.

The steric bulk of phenyl groups could be the reason no apparent relationship could be found between the σ_p values of the para substituents and the binding energy of styrenes to the platinum center. In the presence of PH_3 ligands, however, a linear correlation of r^2 = 0.908 has been found for these two quantities, and even better correlation, r^2 = 0.933, has been obtained between the electrostatic potential in the nucleus of Pt and the ZPE-corrected binding energies of the 4-substituted styrenes (Figure 8). Moreover, invoking charge transfer analysis

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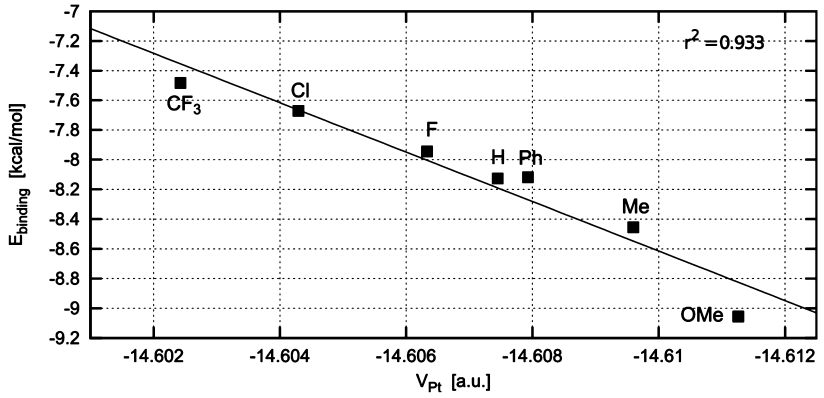

Figure 8. Relationship between the electrostatic potential in the nucleus of Pt in complexes $[HPt(PH_3)_2(olefin)(SnCl_3)]$ and the ZPE-corrected binding energies of para-substituted styrenes.

(CDA), a linear correlation of r^2 = 0.934 has been also found between the σ_p and the amount of back-donation (BD) from Pt to the coordinated olefins. The range of BD is between 0.258 electron for the OMe substituent and 0.279 electron for the most withdrawing CF_3.

These results also emphasize the importance of the thorough examination of substrate electronic effects as well, which is sometimes underrated in comparison to the electronic effect of phosphines and other P-donor ligands.

SUMMARY

As a summary it could be stated that the electronic properties of the 4-substituents of the parent styrene influence the reversal temperature of the enantioselectivity in platinum-(2*S*,4*S*)-BDPP-tin(II) chloride-catalyzed asymmetric hydroformylation. When the electron-donating character of the para substituent is increased, and hence the electron density of the aromatic ring of the substrate, a reversal of enantioselectivity has been observed at lower temperature. Moreover, the presence of electron-donating substituents results in higher branched regioselectivities at higher temperatures in comparison to styrenes containing electron-withdrawing para substituents. These experiments provide further evidence for the reversibility of the Pt-alkyl intermediate formation at higher temperature.

On examination of the electronic structure of the model platinum complex with substituted styrenes, it is found that not only are the electrostatic potentials at nuclei (EPN) of carbons of the coordinating vinyl group directly influenced by the para substituent but also the linear correlation is established between the σ_p and the EPN of all atoms in the coordination sphere of platinum, including the Pt center itself. The consequence of this computational study calls attention to the importance of substrate electronic effects, which may play a role in structure–selectivity relationships equally important as the electronic and steric effects attributed to P-donor ligands.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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