Mechanism for Hydride-Assisted Rearrangement from Ethyldiene to Ethylene in Iridium Cationic Complexes

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The cationic hydride alkylidene complexes \([\text{TpMe}_2\text{Ir}(=\text{CH}−\text{CH}_3)(\text{PM}_{\text{e3}}))^+]\) and \([\text{Cp}^*\text{Ir}(=\text{CH}−\text{CH}_3)(\text{PM}_{\text{e3}}))\) \((\text{TpMe}_2= \text{hydrotris}(3,5\text{-dimethyl-1-pyrazolyl})\text{borate} ; \text{Cp}^* = \text{pentamethylcyclopentadienyl})\) are experimentally known to tautomerize to the corresponding hydride alkene species. Our computational study on the mechanism shows that the reaction takes place through formation of the corresponding alkyl intermediates, with participation of species involving \(\alpha\)- and \(\beta\)-CH agostic interactions. Computed energy barriers reproduce the available experimental kinetic data and agree with a much faster process in the \(\text{Cp}^*\) system. The highest stabilization of the hydride alkylidene complex (the reactant) in the \(\text{TpMe}_2\) system appears as the main reason for the higher barrier found. The difference between the two complexes is due to the steric effects of the spectator ligands.

Introduction

Ligand conversions through hydrogen migration in the coordination sphere of transition metal complexes participate in a large number of common chemical processes, such as \(\alpha\)-C−H and \(\beta\)-C−H additions and eliminations.1,2 Some of the species that may interconvert by means of these processes are transition metal carbene, alkyl, and \(\pi\)-alkene complexes, which are essential intermediates in many organometallic reactions.3,4 The isomerization of a hydride–alkylidene complex \(\text{Ln}(\text{H})\text{M}(\pi\text{-alkene})\) to give the corresponding alkene \(\pi\)-complex \(\text{Ln}(\text{H})\text{M}(\text{alkyl})\) is well documented for cationic electrophilic complexes.5,6 The reverse process is known to take place in early transition metal species,7–10 and in some cases the equilibrium between both complexes has been observed.6,11,12 A typical reaction sequence is shown in Scheme 1. A hydride alkylidene complex is protonated, resulting in hydride alkene species \(a/A\) (labeling scheme explained below), which evolves to the hydride alkene \(e/E\). The presence of a metal–alkyl intermediate seems to be general,13 and the process involves migration of the hydride to the alkylidene and \(\beta\)-hydrogen elimination steps.13–17 The mechanism is further complicated by the possible existence of different alkyl intermediates: \(\alpha\)-agostic (b/B), nonagostic (c/C), or \(\beta\)-agostic (d/D) forms.18–23 The reaction

References

mechanism is interesting by itself, and it can moreover provide insight into the intimately related alkene insertion step in metalloocene polymerization catalysis, where the new bond is not C—H but C—C.25,26

Experimental and computational studies on these rearrangements have illustrated the mechanistic complexity. For \( \text{TpMe}_2\text{Ir}((\text{CH}_3)_2\text{H})(\text{PMe}_3)\),3–7,27 it has been shown that the rate-limiting step is the isomerization between both agostic intermediates. For \([\text{PC} \equiv \text{CP}]\text{RuHCl}\) \([\text{PC} \equiv \text{CP} = N, N'\text{-bis}-(\text{di-tert-butylphosphino})-1,3\text{-diaminopropane})\) and for \((\text{H})_2\text{Zr} = \text{CHCH}_3\),28 the alkene elimination is the rate-limiting step. Other computational work has found that all the possible agostic intermediates need not necessarily be present.29–32 The alkene–alkylidene rearrangement has also been shown to take place without assistance of hydride ligands.33

In this paper we present a computational study of the rearrangement mechanism for two different iridium complexes: \([\text{TpMe}_2\text{Ir}((\text{CH}_3)_2\text{H})(\text{PMe}_3)])^\dagger\) and \([\text{Cp}^\ast\text{Ir}((\text{CH}_3)_2\text{H})(\text{PMe}_3)])^\dagger\). For the \([\text{TpMe}_2\text{Ir}((\text{CH}_3)_2\text{H})(\text{PMe}_3)])^\dagger\) system there are detailed kinetic experimental data available.34 By monitoring the disappearance of the cationic hydride–alkylidene complex at \(-47^\circ\text{C}\), a \(\Delta G^\ddagger\) of 16.7 kcal mol\(^{-1}\) was measured, corresponding to the barrier of the rate-determining step of the whole process, from \(a/A\) to \(e/E\). Additional experiments with deuterated species allowed for deeper insight into the mechanism. Deuteration of the e/E product in CD\(_3\)OD, which is assumed to take place through reactants a/A (requiring the inverse reaction to occur), has a \(\Delta G^\ddagger\) of 25.1 kcal mol\(^{-1}\). The scrambling between deuterium and hydrogen atoms of alkene and hydride in e/E was measured to take place with a \(\Delta G^\ddagger\) of 21.1 kcal mol\(^{-1}\). The \\(\Delta G^\ddagger\) of 25.1 kcal mol\(^{-1}\) for the reverse process lead to a reaction exergonicity close to 8 kcal mol\(^{-1}\). (ii) \(\Delta G^\ddagger\) of 25.1 kcal mol\(^{-1}\) from e/E to a/A and \(\Delta G^\ddagger\) of 21.1 kcal mol\(^{-1}\) from e/E to d/D lead to the estimation that the energy of the transition state between d/D and e/E must be about 4 kcal mol\(^{-1}\) below the rate-determining step for the whole process. The reaction of \([\text{Cp}^\ast\text{Ir}((\text{CH}=\text{CH}_3)(\text{H})(\text{PMe}_3)])^\dagger\) was experimentally studied by similar procedures,35 although the protonation of the hydride–vinyl complex is fast and elucidation of Gibbs energies or detection of intermediates was not possible.

The goal of the present work is twofold. On one hand, we want to validate the general mechanism presented in Scheme 1 and to elucidate the role of alkyl intermediates in the particular case of \([\text{TpMe}_2\text{Ir}((\text{CH}=\text{CH}_3)(\text{H})(\text{PMe}_3)])^\dagger\), for which many experimental data are available. On the other hand, we want to understand the difference between the rates for the two complexes. Comparisons between Tp- and Cp-type ligands can be found regarding H\(_2\) activation, showing that Cp ligands favor the oxidative addition due to the stronger electron-donor character of Cp compared with Tp.35–37 In our case, the reaction is faster for Cp\(^\ast\), contrary to the expectation that this more electron-donating ligand\(^{38}\) should stabilize the carbene, thus slowing the reaction. In our studies, density functional theory (DFT) was used to examine the two complexes of interest. The species presented are named according to the labels in Scheme 1. Lowercase letters a–e are used for the \([\text{TpMe}_2\text{Ir}((\text{CH}=\text{CH}_3)(\text{H})(\text{PMe}_3)])^\dagger\) system, and capital letters A–E for the \([\text{Cp}^\ast\text{Ir}((\text{CH}=\text{CH}_3)(\text{H})(\text{PMe}_3)])^\dagger\) system.

**Computational Details**

Most calculations presented in this paper were carried out with DFT using the B3LYP functional39–41 as implemented in Gaussian 03.42 Both systems \([\text{Cp}^\ast\text{Ir}((\text{CH}=\text{CH}_3)(\text{H})(\text{PMe}_3)])^\dagger\) and \([\text{TpMe}_2\text{Ir}((\text{CH}=\text{CH}_3)(\text{H})(\text{PMe}_3)])^\dagger\) were treated with the standard split-valence polarized 6-31G(d,p) basis set43–45 for all the atoms except the metal center. The LANL2TZ(f) valence basis set46–48 was used for the metal center.
basis set\textsuperscript{16–48} with the associated effective core potentials\textsuperscript{17,49,50} was used for iridium. Frequency calculations were performed to characterize the stationary points. IRC calculations were performed on selected transition states to confirm their connection to the minima. Low-energy conformers associated with rotation of methyl groups of ligands were found in the most sterically crowded complexes. In particular, several conformers within a 1 kcal mol\textsuperscript{-1} range were found for the hydride alkylidene species. Only the most stable one for each species is discussed in the text.

The solvent effect was taken into account by single-point calculations using the polarizability continuum model (PCM),\textsuperscript{51–54} namely, IEF-PCM as implemented in Gaussian 03. Default options were used, except that individual spheres were placed on all hydrogen atoms to get a more accurate cavity. Experimental data had been obtained using a number of solvents: CH\textsubscript{2}Cl\textsubscript{2}, CD\textsubscript{3}OD, and a 4:1 CH\textsubscript{2}Cl\textsubscript{2}/CD\textsubscript{3}OD mixture. In order to relate easily the different steps of the reaction, only one of the experimental solvents, dichloromethane ($\epsilon = 8.93$), was considered. The standard Gibbs energies in dichloromethane ($\Delta G_{\text{sol}}$) were obtained by adding the solvation energies to the gas-phase Gibbs energies computed at 298 K. Reported experimental $\Delta G^\ddagger$ data for the TpMe\textsubscript{2} system were obtained at different temperatures, 226, 273, or 298 K. We decided however to use 298 K in all of our calculations because the goal is not reproducing a given experimental barrier but to provide a compatible reproduction of a given experimental barrier but to provide a compatible entropic contribution of these processes is indeed fairly small (i.e., 0.1 kcal mol\textsuperscript{-1} at 298 K for the rate-limiting step of the TpMe\textsubscript{2} system).

The spin ground state of the 16-electron alkyl intermediate c/C was confirmed to be singlet. The triplet state is 16 kcal mol\textsuperscript{-1} above the singlet for [TpMe\textsubscript{2}Ir(CH\textsubscript{2}CH\textsubscript{3})(PMe\textsubscript{3})]\textsuperscript{–} and 23 kcal mol\textsuperscript{-1} for [Cp*Ir(CH\textsubscript{2}CH\textsubscript{3})(PMe\textsubscript{3})]\textsuperscript{–}. Thus, no spin-state crossings are expected to take place, and singlet species are considered only further on.

B3LYP is a widely used functional, but its accuracy in the reproduction of $\pi$-stacking interactions has been called into question. The problem does not seem to be critical for this system, but the validity of the results was further confirmed by an additional set of geometry optimizations with the hybrid meta-GGA functional MPWB1K.\textsuperscript{55} The key energy barriers were slightly reduced with MPWB1K, but the trends were completely unchanged. For the TpMe\textsubscript{2} system, the gas-phase B3LYP value of 17.9 kcal mol\textsuperscript{-1} for $\Delta E_{TS}$ was reduced to 13.7 kcal mol\textsuperscript{-1} with MPWB1K, and the corresponding values for the Cp* system were 7.8 and 5.7 kcal mol\textsuperscript{-1}, respectively.

**Results and Discussion**

The [TpMe\textsubscript{2}Ir(=CH–CH\textsubscript{3})(H)(PMe\textsubscript{3})]\textsuperscript{+} System. The optimized minima for this system are shown in Scheme 2 and their energies summarized in Figure 1. The starting hydride ethylidene species a presents two rotamers with close energies (0.8 kcal mol\textsuperscript{-1}) differing in the orientation of the ethylidene with respect to the TpMe\textsubscript{2}.

The geometries of these two minima, a\textsubscript{1} and a\textsubscript{2}, are shown in Scheme 2, and they interconvert through transition state ts\textsubscript{a1a2}, which is 8.0 kcal mol\textsuperscript{-1} above a\textsubscript{1}.

Hydrogen migration from iridium to the $\alpha$-carbon of the ethylidene yields the alkyl complex [TpMe\textsubscript{2}Ir(CH\textsubscript{2}–CH\textsubscript{3})(PMe\textsubscript{3})]\textsuperscript{+}. In this case, the $\alpha$- and $\beta$-agostic complexes were found, but nonagostic species were not located. There are two $\alpha$-agostic complexes, b\textsubscript{1} and b\textsubscript{2}, that are connected to a\textsubscript{1} and a\textsubscript{2}, respectively. Their energies are 15.0 and 16.6 kcal mol\textsuperscript{-1} above a\textsubscript{1}, respectively. The agostic nature of these complexes manifests itself in the shortening of the $\alpha$-agostic bond (1.112 Å in b\textsubscript{1}; 1.163 Å in b\textsubscript{2}) and the decrease

\begin{equation}
\text{Scheme 2. Schematic Representation of the Rearrangement of the Hydride–Ethylidene Complex [TpMe}^\text{2}\text{Ir(=CH–CH}_3\text{(H)(PMe}_3\text{)])}^+.\end{equation}
of Ir–C–H angle (98.9° in b1; 79.8° in b2). b2 is the least stable but shows the strongest agostic deformation. This complex has the most favorable arrangement from the electronic point of view, but unfavorable steric repulsions between the phosphine and the alkyl groups. The alkyl complex d presents a β-agostic geometry. This species is much more stable than b1 and b2, being only 4.7 kcal·mol⁻¹ above a1. d has a very long C–H distance of 1.227 Å and a short Ir–H bond length of 1.803 Å. There is no other isomer of d, which is connected to both b1 and b2.

The reaction product e presents a geometry similar to d, where the ethene is twisted, avoiding the sterical bulk of TpMe₂. The computed overall exergonicity from a1 to e is 4.5 kcal·mol⁻¹. This value is also in reasonable agreement with the experimentally estimated exergonicity of 8 kcal·mol⁻¹ (please notice that the experimental estimate is obtained from a measured ΔGᵢ₃₂₃ of 16.7 kcal·mol⁻¹ for the direct process and a measured ΔGᵢ₃₂₉ of 25.1 kcal·mol⁻¹ for the reverse reaction, assuming a small temperature dependence of ΔGᵢ).

The energies of the transition states interconnecting species a, b, d, and e are shown in Figure 1. Since the α-agostic species b1 and b2 are by far the highest-energy intermediates, their associated transition states are also high in energy, and the corresponding reaction steps are rate-determining. The barriers are lower for the transition states associated with b2, tsa2b2, and tsb2d, with energies of 18.4 and 18.5 kcal·mol⁻¹ relative to a1 in both cases. The structure for species tsa2b2, in Figure 2, agrees with the expected concerted formation of the C–H (1.462 Å) bond and cleavage of Ir–H (1.733 Å) and Ir–C (1.919 Å) bonds. The path through b2 is very smooth, because the transition states are only 2 kcal·mol⁻¹ above this intermediate. Transition states associated with b1 are higher in energy (22.7, 21.5 kcal·mol⁻¹) because of the sterical bulk of methyl substituents on the ligands. Our hydride migration barrier (tsa2b2) is in agreement with the barrier of 17.6 kcal·mol⁻¹ computed for the same process on the bidentate system TpMe₂Ir(H)(C₅H₄)(C(CH₃)=CH₂). The transition state tsde, connecting the β-agostic alkyl complex d and product e, has a relative energy of only 5.4 kcal·mol⁻¹ and is just 0.7 kcal·mol⁻¹ above d.

The lowest-energy reaction pathway from the hydride–alkylidene complex a1 to the hydride–alkene complex e goes through species tsa1a2, a2, tsa2b2, b2, tsb2d, d, and tsde (see Figure 1). This process has an overall barrier ΔGᵢ₃₂₉ of 18.5 kcal·mol⁻¹, which is in excellent agreement with the experimentally measured ΔGᵢ₃₂₃ of 16.7 kcal·mol⁻¹. The highest-energy transition state tsb2d, which corresponds to the conversion from the α-agostic intermediate to the β-agostic one, is nearly equal in energy to the transition state tsa2b2 corresponding to the hydride migration. The ΔGᵢ₃₂₉ value of 23.0 kcal·mol⁻¹ computed for the reverse, e → a, process is slightly lower but in good agreement with the experimentally measured value of ΔGᵢ₃₂₉ of 25.1 kcal·mol⁻¹.

There is a serious difference in the experimental assignment of the barrier from e to d. It was estimated experimentally to be ΔGᵢ₃₂₇ of 21.1 kcal·mol⁻¹ relative to e, while in our calculations tsde is only 9.9 kcal·mol⁻¹ above e (at 298 K). However, this discrepancy can be easily explained taking into account that the experiment measured the rate of scrambling between a deuterated alkene and the hydride in e. This scrambling obviously requires the conversion from e to d through tsde, but it also requires the internal rotation of the β-methyl of the alkyl to make its hydrogens equivalent. The computed transition state tsrot for this second process is 20.2 kcal·mol⁻¹ above e. Thus, agreement with all measured experimental barriers was accomplished, providing strong support for the proposed mechanism.

A hypothetical alternative mechanism, the direct 1,2-hydrogen shift within the hydrocarbon ligand, i.e., without metal participation, was discarded, since the corresponding computed transition state is at 34.4 kcal·mol⁻¹ above a1 in terms of ΔGᵢ₃₂₉ in the gas phase, which is prohibitively high. A similar behavior was reported previously for the TpMe₂Ir-(H)(α-C₅H₄)(C(CH₃)=CH₂) system.

The [Cp*Ir(=CH–CH₂)(H)(PMe₃)]⁺ System. [Cp*Ir(=CH–CH₂)(H)(PMe₃)]⁺, obtained by protonation of the [Cp*Ir(=CH–CH₂)(H)(PMe₃)], also yields a hydride–alkene complex. However, in this case no intermediates were experimentally detected at −80 °C, indicating an overall reaction faster than in the previously studied system.

The computed local minima are presented in Scheme 3, and their energies are given in Figure 3. Qualitatively, this system is similar to the [TpMe₂Ir(=CH–CH₂)(H)(PMe₃)]⁺ one. Thus, it will be discussed in less detail, highlighting only the differences. The α-agostic (B) and the nonagostic (C) alkyl complexes are 0.4 and 1.0 kcal·mol⁻¹ above A1, respectively, while the β-agostic (D) is 0.3 kcal·mol⁻¹ below A1. In the nonagostic species C the Ir–C–H angle is 107.3° as compared with 100.6° in the α-agostic complex B. The product E is connected directly only to D and has an energy 13.6 kcal·mol⁻¹ below A1. The transition state connecting the alkyl D to E has an energy 1.4 kcal·mol⁻¹ below that of D on the ΔGᵢ₃₂₉ scale, which means that the D → E conversion is barrierless at room temperature.
The preferred reaction pathway from A1 to E goes through intermediates B, C, and D. The rate-limiting step is the α-H migration through transition state tsA1B (see Figure 2), with a barrier of only 7.4 kcal mol\(^{-1}\) above A1. The C–H, Ir–C, and Ir–H distances of 1.605, 1.927, and 1.675 Å, respectively, are consistent with the fact that tsA1B is a transition state for hydride migration. The low barrier is in full agreement with the experimental observation of a fast process. From A2 there are two reaction pathways with similar barriers slightly above 11 kcal mol\(^{-1}\), via C or via A1 formation.

Similarly to the [Tp\(^{Me}\)Ir(=CH–CH\(_3\))(H)(PMe\(_3\))]\(^+\) system, the direct 1,2-hydrogen shift without metal participation has a prohibitively high \(\Delta G^\circ_{298}\) barrier of 35.1 kcal mol\(^{-1}\) in the gas phase.

**Comparison between the [Tp\(^{Me}\)Ir(=CH–CH\(_3\))(H)(PMe\(_3\))]\(^+\) and [Cp\(^*\)Ir(=CH–CH\(_3\))(H)(PMe\(_3\))]\(^+\) Systems.** For the system with Tp\(^{Me}\), the highest-energy transition state tsb2d corresponds to the conversion from the α-agnostic to the β-agnostic intermediate, although the transition state ts2b2 for the hydride migration is located only 0.1 kcal mol\(^{-1}\) below. For the system with Cp\(^*\), the rate-limiting step corresponds to the hydride migration through transition state tsA1B. There is a change in the rate-limiting step between the two systems, but this seems to have little chemical relevance.

The critical difference between the two systems, which affects the chemical behavior, is the barrier between the reactant and the rate-determining transition state. The value is 18.5 kcal mol\(^{-1}\) for the Tp\(^{Me}\) system and 7.4 kcal mol\(^{-1}\) for the Cp\(^*\) system, with a difference of about 10 kcal mol\(^{-1}\). Interestingly, the barriers for the inverse reaction, which would be endergonic, are much closer, with values of 23.0 and 21.0 kcal mol\(^{-1}\), respectively. Comparison of reaction profiles (Figures 1 and 3) clearly shows that the main difference between the two systems is in the relative energies of the starting species, a/A: with reference to e/E, a1 and a2 have a much lower energy in the Tp\(^{Me}\) system than A1 and A2 in the Cp\(^*\) system. This is, for instance, reflected in \(\Delta G^\circ_{298}\) for the entire process (a/A < e/E), which is −4.5 kcal mol\(^{-1}\) for the Tp\(^{Me}\) system and −13.6 kcal mol\(^{-1}\) for the Cp\(^*\) system.

The role of steric effects in the reactivity of the system was further elucidated by additional calculations, in which a, e, A, and E were reoptimized after replacing the methyls of the Tp\(^{Me}\), Cp\(^*\), and PMe\(_3\) ligands by hydrogen atoms. These species with Tp, Cp, and PH\(_3\) ligands are labeled as a–h, e–h, A–h, and E–h. The difference in energy between a–h and e–h is −10.4 kcal mol\(^{-1}\) (a–h − e–h), that between A–h and E–h is −9.2 kcal mol\(^{-1}\)(A–h − E–h). Therefore, suppression of steric effects makes the systems much more similar. Without steric effects the reaction would become slightly more exergonic (1.2 kcal mol\(^{-1}\)) for the Tp-derived ligand, as could be expected from purely electronic effects.\(^{(56)}\)

To further analyze the difference in stability between the two metal–alkylidene complexes a1 and A1, the metal–carbene binding energy was computed for both species and decomposed in distortion and interaction terms, following an approach already employed by some of us to investigate different coordination modes of one ligand.\(^{(57,56)}\)

The binding energy that results from the formation of complexes a1 and A1 from the fragments ([Tp\(^{Me}\)Ir(H)(PMe\(_3\))]\(^+\)) or [Cp\(^*\)Ir(H)(PMe\(_3\))]\(^+\) and CHCH\(_3\)) in their optimized isolated geometries has been determined as arising from the combination of two terms. One is the distortion of the fragments from their free geometries to those they adopt in the complexes (\(\Delta E_{\text{dist}}\)) and the other the interaction energy that stems from the combination of the two fragments to give the real complexes (\(\Delta E_{\text{int}}\)). The results are summarized in Scheme 4. The alkylidene is strongly bonded in both systems,\(^{(57)}\) as shown by the high values of the binding energies (102.9 and 98.4 kcal mol\(^{-1}\) for the Tp\(^{Me}\) and Cp\(^*\) complexes, respectively). In agreement with the higher stability of the metal–alkylidene in the Tp\(^{Me}\) complex, the M=CC bond energy of the Tp\(^{Me}\) system a1 is 4.5 kcal mol\(^{-1}\) larger than that of the Cp\(^*\) system A1. This difference is mainly retrieved in the distortion term of the metal fragment since this...
The steric requirements in the rest of the complexes fit better with the Cp* pattern because the steric pressure of the ligands is not concentrated in a specific region. For instance, the transition state tsab presents the hydride approaching the alkylidene to form b, a movement sterically hindered because of the proximity of the hanging methyls of TpMe 2. The case of the β-agostic complexes dB/D is somewhat special because of the more compact arrangement of the ligand. In this case, the relative energies with respect to the reactants are more similar (4.7 kcal·mol⁻¹ for d → a1, −0.3 kcal·mol⁻¹ for D → A1).

Conclusions

Our computational study on the ligand rearrangement in the [TpMe 2Ir(═CH−CH₃)(H)(PMe₃)]⁺ and [Cp*Ir(═CH−CH₃)(H)(PMe₃)]⁺ systems reproduces accurately the available experimental kinetic data on the reactivity of these species. The results confirm the validity of the previously proposed mechanism involving active participation of the hydride ligand and going through intermediates containing alkyl ligands stabilized by agostic interactions. The computed barriers are 18.5 and 7.4 kcal·mol⁻¹, respectively, indicating a much faster reaction for the [Cp*Ir(═CH−CH₃)(H)(PMe₃)]⁺ system, in agreement with experiment.

The different reaction rates for the two complexes can be attributed to differences in steric effects and flexibility. TpMe 2 presents the pyrazolyl methyl groups close to the other ligands, hindering addition of the α-H bond and alkyl rotation. At the same time, the space between the methyl groups is sufficient to accommodate the alkylidene ligand, thus stabilizing the reactant complex. The steric effect of the Cp* is more uniform in space and conserved throughout the process. The electronic effects seem to play a minor role in the difference between these systems.

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Supporting Information Available: Scheme S1, Cartesian coordinates, and absolute energies of all presented species are available free of charge via the Internet at http://pubs.acs.org.