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Modelling Me_5C_5 for reactivity studies in $(\eta^5\text{-}C_5Me_5)_2Ln–R$: full DFT and QM/MM approaches

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DFT (B3PW91) and QM/MM (ONIOM) calculations have been carried out to compare several models of the cyclopentadienyl ligand (L) for the insertion of ethylene into the Ln–C bond of $L_2Ln–Et$ and β-H transfer to the incoming monomer. Calculations have been carried out for C_5Me_5 (Cp*) where all atoms are explicitly treated at the DFT level, for C_5Me_5 ($Cp^{\#}$) at the QM/MM (B3PW91:UFF) level where the Me groups are taken into account by a molecular force field, C_5H_5 (Cp) and Cl. Comparisons of these systems provide information about the stereoelectronic effects of the ligands on the elementary steps of the reaction. Although $Cp^{\#}$ has the steric properties of Cp* but the electronic properties of Cp, the geometry and energy barriers are very close for Cp* and $Cp^{\#}$ suggesting that steric effects outweigh the electronic effects of the Me groups of the cyclopentadienyl ligand.

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Introduction

Modelling ligands is a central concern for reactivity studies of large organometallic complexes. It is tempting to use brute force DFT calculations on the complete experimental system because these can be carried out at manageable computational cost even for large systems. However, such an approach is not entirely satisfying. First, whilst a long calculation can be considered for some well-chosen chemical systems, it can get out of hand when a large number of calculations are needed. Even more important, computational studies can give insights into the electronic/steric roles played by a ligand in a given complex for representative elementary reaction steps.

This study focuses on cyclopentadienyl ligands in lanthanocenes. Substituents on cyclopentadienyl have very often been ignored and calculations have been carried out with C_5H_5 (Cp) with overall good qualitative results. However, this may be a invalid approximation as shown, in particular, in a detailed study of ring substitution in some zirconocene complexes.[1] The average of the symmetric and asymmetric stretches of $(Cp^R)_2Zr(CO)_2$ (R = Me, Et, Pr^i, Bu^t, $SiMe_3$) shows a good correlation with Hammet σ_{meta} parameters, thereby suggesting an influence of R *via* a simple inductive effect. In contrast, the reduction potentials (E^0) of $(Cp^R)_2ZrCl_2$ do not correlate with σ_{meta}, suggesting that factors other than the substituent inductive effect influence E^0. The R substituents also influence the geometry of the metallocene, notably the angles between the cyclopentadienyl rings as well the $Cp_{centroid}–M–Cp_{centroid}$ (X–M–X) angle. Substituents R can therefore influence an energy barrier in an unexpected manner.

Few systematic comparisons of the influence of the ring substituent or of the model of the whole ligand on the reactivity have been carried out. Earlier studies have used Cl to model the cyclopentadienyl ring because these two ligands are isolobal. Despite some success limitations have been noted: Cp has been found to be more donating than Cl.[2–4] Recently, the metathesis reaction of L_2MCH_3 (L = H, Cl, C_5H_5, C_5Me_5; M = Y, Sc, Lu) has been studied.[5] The influence of L (C_5H_5 and C_5Me_5) on the interaction of lanthanocene L_2M with ligands such as H_2, N_2, C_2H_4 and alkyne has been studied.[6] These studies show that the electrophilicity of L decreases in the order Cl, C_5H_5, C_5Me_5. In addition, the steric bulk of C_5Me_5 further weakens the interaction of the lanthanocene with any substrate.

The ability of ethylene to insert into the M–R bond of L_2MR is the key to the reactivity of this family of complexes, which are used as polymerization catalysts.[7] For this reason, a number of theoretical studies have been carried out on the reactivity of d^0 metallocene derivatives.[8] A large number of computational studies, mostly focused on group IV metals, have analyzed several aspects of the olefin polymerization process.[9] In this paper, we focus on the influence of L on ethylene insertion into the M–Et bond of $L_2Ln–Et$ monomer as a function of L, shown in eqn. (1):

$$L_2Nd–Et + C_2H_4 \rightarrow L_2Nd\text{-}n\text{-}Bu \qquad (1)$$

We also look at the H exchange between the ethyl and ethylene ligands *via* β-H transfer, shown in eqn. (2):

$$L_2Nd–C_2H_5 + C_2\mathit{H}_4 \rightarrow L_2Nd–C_2\mathit{H}_4H + C_2H_4 \qquad (2)$$

Nd has been chosen for the lanthanide centre. X has been chosen to be Cl, C_5H_5 or C_5Me_5, the latter being explicitly treated by DFT (Cp*) or with a hybrid QM/MM approach ($Cp^{\#}$). In the $Cp^{\#}$ model, the Me groups are part of the MM level and thus play an exclusively steric role, the electronic effect of $Cp^{\#}$ being that of Cp. The numbering of atoms is given in Chart 1.

Computational details

The large core Relativistic Effective Core Potential (RECP), optimized by the Stuttgart–Bonn group,[10] has been shown to be well-adapted to the computation of lanthanides complexes

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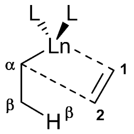

Chart 1

since 4f electrons do not participate in metal-ligand bonding.[11] Basis sets adapted to the RECP's augmented by a polarization f function (exp = 1.000) have been used for Nd. Cl has been also represented with an ECP and the associated basis set[12] augmented by a d polarization function (exp = 0.643).[13] Carbon and hydrogen have been represented with an all-electron, double-ζ quality, 6-31G(d,p) basis set and C and H atoms of the Me groups of the Cp* ligands with an all electron, double-ζ quality, 3-21G(d,p) basis set when treated by quantum mechanics.[14] Calculations were carried out at the hybrid DFT level of theory using the functional B3PW91.[15] The two -layer ONIOM calculations were carried out at the B3PW91/UFF level using nearby Pr in place of Nd for technical reasons.[16] This change should have no consequences due to the very weak influence of the nature of the metal on the potential energy surfaces.[4,17] Geometry optimizations have been carried out without any symmetry restrictions. The nature of the extrema obtained with the DFT and ONIOM calculations has been verified by analytical frequency calculations. Zero-point energy (ZPE) and entropy contributions have been calculated from the approximation of harmonic frequencies. The free enthalpy energies *G* are given at 298.15 K. The connectivity of each transition state has been checked while following the intrinsic reaction coordinate (IRC). All the calculations have been carried with the Gaussian98 suite of programs.[18]

Results

$CH_2{=}CH_2$ and $Cl_2Nd–Et$

Tricoordinate LnX_3 is pyramidal unless X is a good π-donor ligand.[19] Accordingly, $Cl_2Nd–Et$ is pyramidal with a significantly elongated β-C–H agostic bond (1.141 Å) and a Nd–C(α)–C(β) angle equal to 91.2°. Because of the large radius of the lanthanide ion, there is enough space for coordination of an ethylene. With only some small structural changes, ethylene can coordinate cis (front-side attack, "fs") or trans (back-side attack, "bs") to the agostic bond.[9] The free energy profile is shown in Fig. 1 and the energies summarized in Table 1. The structural features of L_2NdEt and $L_2Nd–n\text{-}Bu$ are given in Table 2. The bonding interaction between the metal fragment and ethylene is small since the free energies of coordination of ethylene are 2.1 and 3.2 kcal mol^{-1} for the bs and fs approaches, respectively (complexes fs-A_{Cl} and bs-A_{Cl}). The geometries of the two adducts are different but the very ionic bonding in lanthanide complexes does not induce strongly directional bonding, hence the similar energies. The two adducts maintain the β-C–H agostic interaction. The activation barriers for insertion are 7.2 and 7.9 kcal mol^{-1} for the fs and bs approaches. Therefore, the more stable adduct is also associated with the slightly preferred transition state. The fs transition state, fs-TS_{Cl}, connects to a *n*-butyl complex with no agostic interaction but a slight conformational change in the *n*-butyl chain gives a β-C–H agostic interaction, 1 kcal mol^{-1} more stable than the non-agostic structure. We will thus consider only the insertion product with the β-C–H agostic bond. The insertion reaction is exothermic by 13.9 kcal mol^{-1}, as expected from the replacement of a C=C double bond by a C–C single bond.

Table 1 Free energies of reaction ($\Delta_rG°$/kcal mol^{-1})[a] for the front side (fs) ethylene insertion into L_2NdEt.

	Cl	Cp	Cp$^{\#b}$	Cp^{*c}
$\Delta_rG°_{cplx}$	−3.2	5.2	10.9	10.5
$\Delta_rG^{\#}_{ins}$	7.2	13.0	15.1	16.1
$\Delta_rG°$	−13.9	−13.3	−12.4	−12.3
$\Delta_rG^{\#}_{trf}$	12.4	21.0	27.7	25.8

[a] The ins and trf subscripts refer to the insertion and transfer reactions, respectively. The subscript cplx refers to the ethylene adduct. [b] B3PW91/UFF ONIOM calculation [c] Full DFT calculations

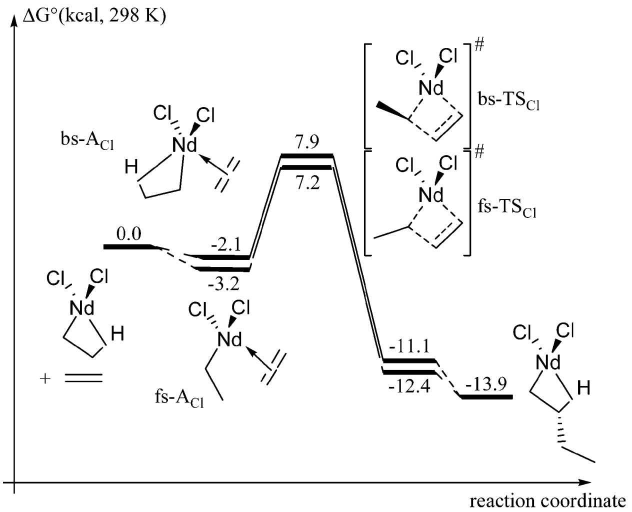

Fig. 1 Free energy profiles (kcal mol^{-1}) for the insertion of ethylene into the Ln–C bond of $Cl_2Ln–Et$ for front-side (fs) and back-side (bs) approaches.

The geometries of the transition states (TS) for fs and bs approaches are significantly different. In fs-TS_{Cl}, the Nd–ethyl moiety is almost linear whereas it is significantly bent in bs-TS_{Cl}. The C···C distance of the bond being formed is 2.242 and 2.313 Å for bs- and fs-TS_{Cl}, respectively. The former TS has a β-agostic C–H bond and the latter has none. fs-TS_{Cl} has the incoming olefin and alkyl chain all in one plane, which probably insures the best overlap between the carbon lone pair of the ethyl ligand in the ethylene π* orbital. Despite their geometrical differences, fs-TS_{Cl} and bs-TS_{Cl} are energetically close with a slight preference for the front-side approach. Because our study is not focused on the particularities of the insertion reaction itself but on how the ligands on the metal change the geometrical and energetic features of a representative reaction in lanthanide chemistry, we have thus selected the fs attack to look at the consequences of changing Cl to Cp, Cp# and Cp*.

The β-H transfer reaction is an athermic reaction since it just exchanges ethyl and ethylene. The transition state has C_s symmetry and the activation barrier has been calculated to be 12.4 kcal·mol^{-1}, which is significantly higher than the barrier for ethylene insertion.[9] At the transition state the C–H bond to be formed and broken is long (1.514 Å) and Nd–H is rather short (2.815 Å). The C^{β}–H–$C^{\beta'}$ angle is widely open to 166.6°. The Nd–C^{α} distance (2.581 Å) is shorter than Nd–C^{β} (2.815 Å). The two ethylene groups are thus side-bonded to an elongated Nd–H bond. A negative charge is delocalized on the two ethylenic moieties as well as on the hydride. In this way the interaction between the positively charged Nd centre and the entire hydrocarbyl part is strong.

Influence of L = Cl, Cp, Cp# and Cp*

The energies for the fs insertion of ethylene in the Nd–C bond of $L_2Nd–Et$ are given in Table 1 and the energy profile is schematically represented in Fig. 2 for L = Cp, Cp# and Cp*. $\Delta_rG°_{cplx}$ is the free energy of coordination of ethylene to L_2NdEt, $\Delta_rG^{\#}_{ins}$ and $\Delta_rG^{\#}_{trf}$ are respectively the activation barriers of the insertion and β-H transfer with respect to the separated reactants, $\Delta_rG°$ is the free energy of reaction for the

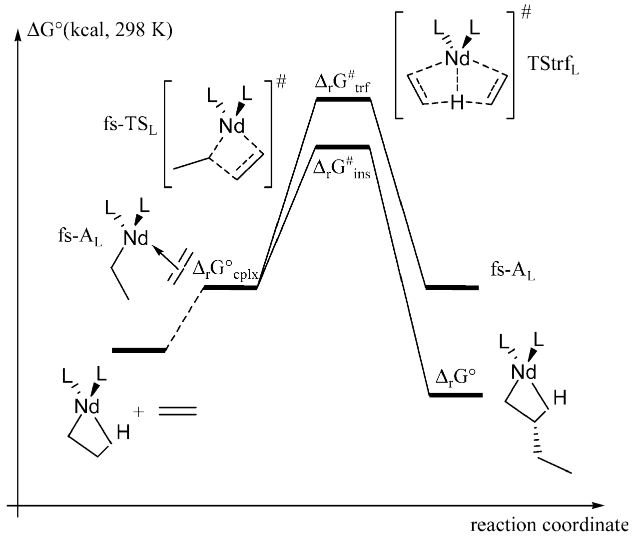

Fig. 2 Qualitative free energy profile for insertion of ethylene in the Ln–C bond of L_2Ln–Et for front-side (fs) approach and for β-H transfer. All values are given in Table 1.

insertion reaction. There are significant differences between the energy profiles for L = Cl and the cyclopentadienyl models. Coordination of ethylene is slightly exothermic for X = Cl but is endothermic for all Cp type ligands. The energies of reaction for all types of L are essentially equal and the slightly smaller values of Δ_rG° in the cases of Cp and Cp* are only due to the lack of the agostic interaction in the *n*-butyl complex.† The lack of influence of L on Δ_rG° can be expected from the fact that the energy of reaction is essentially characteristic of the loss of the C=C π bond and the making of the C–C single bond and only marginally on the nature of the metal centre. In contrast, the activation barriers $\Delta_rG^\#_{ins}$ differ significantly and increase from Cl to Cp*. The activation barrier for β-H transfer is also much smaller for Cl than for any Cp-type ligand. At this point, we note that Cl gives significantly different results from Cp-type ligands and that there are smaller but not negligible differences between the various Cp models.

The influence of L on the geometrical parameters of the ethyl and *n*-butyl complexes is given in Table 2. The Nd–C^α bond length increases in the order Cl < Cp < Cp* < $Cp^\#$. This trend is well-accounted by the variation in the Mulliken charge at the metal centre (Table 3): the electronegative chlorine gives the highest positive charge to Nd and the positive charge decreases from Cp to Cp*. It is thus interesting to note that the longest Nd–C^α bond, found for $Cp^\#$, cannot be attributed to an electronic effect (almost equal charges for Cp and $Cp^\#$) but to a subtle change in the steric factors. The change in the coordination sphere is represented in great part by the variation in the X–Nd–X angle, where X is either Cl or the cyclopentadienyl centroid. The X–Nd–X angle increases significantly from Cl to Cp* but is almost equal for $Cp^\#$ and Cp*, indicating that the steric factor also determines the angle. Bending the X–M–X angle increases the bonding ability of the metal towards other ligands. This is another contributor to the increase of the Nd–C^α distance when going from Cl to Cp*.

Table 2 Structural parameters of L_2Nd–R. Distances are in Å and angles in degrees.

R	L	Nd–C^α	C^α–C^β	C^β–H^β	X–Nd–X^a	Nd–C^α–C^β
Et	Cl	2.388	1.522	1.141	123.4	91.2
	Cp	2.473	1.518	1.142	138.5	89.5
	$Cp^\#$	2.489	1.519	1.141	141.8	89.5
	Cp*	2.474	1.521	1.138	143.8	90.0
n-Bu	Cl	2.390	1.521	1.151	124.0	91.2
	Cp	2.476	1.518	1.147	137.9	90.0
	$Cp^{\#b}$	2.529	1.536	1.099	140.6	115.9
	Cp*	2.525	1.536	1.100	140.9	114.0

^{a} X is the centroid of the cyclopentadienyl ring; for Cl, X = Cl ^{b} See †.

Table 3 Mulliken charge on Nd in L_2LnEt and TS_L

L	Cp_2NdEt	fs-TS_L
Cl	1.392	1.305
Cp	0.837	0.741
$Cp^\#$	0.829	0.769
Cp*	0.707	0.593

The nature of L has essentially no influence on the C^α–C^β distance. It is more remarkable that it has only a marginal influence on the length of the β-C–H agostic bond, which is present in all systems.† Two types of electronic factors lengthen the β-C–H bond: one is the delocalization of the carbon C^α lone pair in the adjacent bonds,[19,20] the other is the traditional donation from the C–H bond to the empty metal coordination sites.[21] A strong positive charge on the metal favours the latter over the former and a small positive charge gives more importance to the first effect. An approximate compensation is thus to be expected.

Coordination of the ethylene to L_2Nd–Et is endothermic for all Cp-type ligands (Table 1). An olefin binds only weakly to a metal deprived of back-bonding capability but increasing electrophilicity increases the bond dissociation energy. This is why ethylene binds more strongly to Nd for L = Cl than for any cyclopentadienyl model. Entropy favours dissociation, which results in a positive $\Delta_rG^\circ_{cplx}$. The free energy of coordination is significantly more unfavourable for $Cp^\#$ and Cp* than for Cp and is almost equal for $Cp^\#$ and Cp*. Since $Cp^\#$ has the electronic characteristics of Cp but the steric and geometrical features of Cp*, this suggests a key role played by the steric and geometrical parameters in determining the difference between Cp* and Cp, at least for this problem.

The structural features of $L_2NdEt(\eta^2\text{-}C_2H_4)$ (fs-A_L) are given in Table 4 and the associated relative free energies are given in Table 1. The β-C–H agostic bond is present in the adduct of $Cl_2NdEt(\eta^2\text{-}C_2H_4)$ (fs-A_{Cl}) and also in $Cp_2NdEt(\eta^2\text{-}C_2H_4)$ (fs-A_{Cp}) but not in $Cp^\#_2NdEt(\eta^2\text{-}C_2H_4)$ (fs-$A_{Cp^\#}$) and $Cp^*_2NdEt(\eta^2\text{-}C_2H_4)$ (fs-A_{Cp^*}). A combination of lack of space in the wedge between the bulky $Cp^\#$ or Cp* ligands and decreasing bonding capability with increasing X–Nd–X angle disfavours the weak agostic interaction. The energy consequence for the lack of agostic interaction is no more than 1 kcal mol^{-1} and is thus not determinant for the energy profile. Thus, the variation in the Nd–C^α–C^β angle from 90° to 140° has no energy consequence.

The activation energy for ethylene insertion in the Nd–Et bond increases notably in the order Cl << Cp < $Cp^\#$ $\lesssim$ Cp* relative to separated reactants (Table 1). The biggest difference is between Cl and Cp but Cp gives a significantly smaller activation barrier than $Cp^\#$ and Cp*, which give similar barriers. In no case is the energy barrier high enough to make the reaction difficult.

The structural features of the transition states of the ethylene insertion (from a front-side attack) in the Nd–Et bond of L_2NdEt (fs-TS_L) are given in Table 4. The incipient C(2)···C^α bond is close for all L and averages 2.3 Å. The other differences in the structural features associated with the

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† The *n*-butyl complex given in this study is that obtained by the descent from the transition state for ethylene insertion and has no β-C–H agostic interaction. A minor conformation change permits the establishment of the β-C–H agostic interaction. It has been shown in the case of Cl_2Nd–Et that the agostic and non-agostic structures differ by only 1 kcal mol^{-1}. Therefore no additional search for the conformation with the β-C–H agostic interaction was carried out.

Table 4 Structural parameters of $L_2Nd(Et)(C_2H_4)$, fs-A_L, and for the associated transition state fs-TS_L. Distances are in Å and angles in degrees.

Structure	Nd–C^α	C^α–C^β	C^β–H^β	Nd–C(1)	C(2)···C^α	C(1)–C(2)	C(1)–C(2)–C^α	X–Nd–X[a]	Nd–C^α–C^β
fs-A_{Cl}	2.415	1.510	1.144	2.915	4.512	1.346	100.3	122.6	91.3
fs-A_{Cp}	2.489	1.511	1.139	3.077	4.516	1.342	106.1	132.7	90.8
fs-$A_{Cp^\#}$[b]	2.536	1.526	1.097	3.083	2.876	1.347	125.1	136.5	143.4
fs-A_{Cp^*}[b]	2.528	1.526	1.098	3.006	3.056	1.344	123.8	138.5	137.9
fs-TS_{Cl}	2.454	1.514	1.096	2.544	2.313	1.393	121.1	127.7	166.3
fs-TS_{Cp}	2.558	1.516	1.098	2.606	2.251	1.397	124.0	132.7	156.4
fs-$TS_{Cp^\#}$[b]	2.585	1.518	1.098	2.660	2.294	1.389	123.6	137.6	155.3
fs-TS_{Cp^*}[b]	2.560	1.516	1.098	2.626	2.296	1.391	124.0	138.4	159.4

[b] No β C–H agostic bond [a] X is the centroid of the cyclopentadienyl ring; for Cl, X = Cl

change in L, in particular the X–Nd–X angle, are equivalent to that in the adducts or in the starting alkyl reactants. The Mulliken charge at Nd varies as in L_2NdEt (Table 3). There is major electronic reorganization as expected from this type of reaction. This suggests that the electronic factors that stabilize the ethylene adducts also lower the activation energies of insertion. The difference in energy between the transition states and the adducts is 10, 7.8, 4.2 and 5.6 kcal mol^{-1} for Cl, Cp, Cp# and Cp*, respectively. Thus, it is not the insertion step that becomes more difficult when going from Cl to Cp*. In fact, the insertion step becomes significantly easier. It is remarkable that these differences in energies are very close for Cl and Cp, on the one hand, and Cp$^\#$ and Cp*, on the other hand, with a significant decrease in value for the latter. The small values for the more bulky model of cyclopentadienyl are related to the steric relief associated with the insertion. The higher barrier for Cl reflects the fact that the ethylene is more tightly bonded in the adduct. Whilst the total activation energies are relatively close for all Cp models, the nature of the ligand influences in a subtle way the energy pattern between extrema.

The activation energy for the β-H transfer almost doubles when replacing Cl by Cp. The energy barrier increases only slightly when Cp is changed into Cp$^\#$ or Cp*. However, the geometrical parameters of the transition states, $TStrf_L$, are rather similar for all L (Table 5).

Discussion

The energy profiles for Cl are sufficiently different from any model of the cyclopentadienyl ligand to show some significant limitations in using the former ligand for quantitative study of mechanisms. However, the structural parameters for all intermediates and transition states are sufficiently similar for all L to justify the use of exploratory calculations having Cl as the ligand.

The comparison between Cp, Cp$^\#$ and Cp* is informative on the role played by the methyl groups. Cp and Cp$^\#$ have the same electronic features whereas Cp$^\#$ and Cp* have the same steric features. For the systems and reactions under consideration, the energy profiles are close for Cp* and Cp$^\#$ and both slightly differ from that for Cp. The analysis of the results shows that the geometrical features for Cp$^\#$ and Cp* are very close and are somewhat different for Cp. These features are thus determined by the steric features imposed by the methyl groups. The ligands influence the characteristics of the wedge between the two Cp rings. In the case of Cp$^\#$ and Cp* the wedges are similar because of the identical size of the two L groups.

The activation energy increases from Cl to Cp* relative to separated reactants for the cyclopentadienyl derivative could suggest that the insertion reaction is disfavoured by the electron-donating ligand L. However, the free energy difference between the transition state and the ethylene adduct suggests the opposite since it decreases from Cl to Cp and Cp$^\#$ or Cp* (very similar for these two ligands), that is, decreasing the stability of the olefin complex favours the insertion step. The relative influence of L depends on the nature of the reaction. The nature of L influences more the coordination of the olefin than the transition state for the insertion reaction. Whilst Cl favours the ethylene coordination, all models of cyclopentadienyl disfavour it. Furthermore, permethylcyclopentadienyl disfavours coordination of ethylene from a combination of steric and electronic factors. The unfavourable influence of Me on the coordination to lanthanide has been already noted in the case of lanthanocene complexes for a variety of ligands such as H_2, N_2, C_2H_4 and C_2R_2.[6] The same effect applies to a Ln^{III} metal centre. Thus, Cl is a poor model overall, Cp appears to be an acceptable model for a substituted cyclopentadienyl group if the coordination around the metal is not modified, but is less reliable for study of the coordination of a ligand. This can have important consequences for elementary steps starting with pre-coordination of the incoming ligand. The influence of L in the β-H transfer illustrates this point. Using Cl in place of a cyclopentadienyl ring for the β-H transfer results in a very poor reproduction of the energy profile calculated with cyclopentadienyl ligands. The activation energy almost doubles going from Cl to Cp but the increase in the activation energy is more moderate with the other models of the cyclopentadienyl ring. The transition state is made of a hydride transferring between two ethylenes coordinated to the metal. The coordination of the ethylene is much less favourable in the presence of a Cp ring than in the presence of a Cl ligand, due to a combination of charge and steric factors. The energy of the transition state that has two olefins coordinated is thus going to be even more sensitive to the nature of the ancillary ligand. Steric factors are also more important because the olefin ligands are pushed towards the narrow end of the wedge. Using Cl in place of Cp in comparing the insertion and the β-H transfer would thus result in a wrong energy estimate of two possibly competing reactions. This could be a major weakness for the study of a catalytic process.

Table 5 Structural parameters for the β-H transfer transition state, $TStrf_L$, which has C_s symmetry. Distances are given in Å and angles in degrees.

L	Nd–C^α	Nd–C^β	Nd–H	C^α–C^β	C^β–H^β	C^β–H^β–$C^{\beta'}$	C^α–Nd–$C^{\alpha'}$	X–Nd–X[a]
Cl	2.581	2.815	2.204	1.405	1.514	166.6	124.1	125.6
Cp	2.667	2.866	2.234	1.404	1.498	163.3	120.6	132.1
Cp$^\#$	2.716	2.899	2.253	1.404	1.484	160.6	117.8	136.7
Cp*	2.671	2.870	2.240	1.404	1.482	162.4	119.6	138.6

[a] X is the centroid of the cyclopentadienyl ring; for Cl, X = Cl.

The QM/MM model of the permethylcyclopentadienyl ring performs remarkably well. The structural features and energy profiles are very close to those obtained with the full DFT model of C_5Me_5. This suggests that the methyl groups modify the coordination of the 5-membered ring mostly for steric reasons. The X–Nd–X angles are very close for $Cp^{\#}$ and Cp* and this determines the bonding properties of the metal towards other ligands and thus the energy pattern. Thus, the "steric" effects of permethylcyclopentadienyl is not limited to the direct interaction between the incoming reagent and the Cp* group but also to a subtle change of bonding properties at the metal centre. For instance, increasing the X–M–X angle decreases the distance between Cp* and the incoming ligand but also diminishes the bonding ability of the metal itself. The decrease of the metal-ligand interaction in metallocene complexes upon replacement of Cp by Cp* has been shown for several types of ligands.[6] Even if there is no doubt that the methyl groups make the cyclopentadienyl a slightly better electron donor, this does not seem to have a leading role in the energy profiles of the reactions studied here. Generalization of these effects needs extra precautions. Substitution at the cyclopentadienyl ring can influence the physical responses of the metal as has been shown by Bercaw, Green *et al.*[1] and is best interpreted in terms of increased electron-donating ability associated with the Me substituent. We show here a slightly more complex situation.

What is the best model of cyclopentadienyl ring for computational studies? Cl is without doubt a very poor model but can be used for exploratory calculations; Cp is certainly an acceptable model, much less computationally expensive than full quantum C_5Me_5. The QM/MM model $Cp^{\#}$ performs remarkably well and is certainly a model of choice, a good compromise between chemical relevance and computational expense. These studies show also that the dependence on the model in turn depends on the reaction. However, the QM/MM model has so far given results very close to the full DFT computations.

The present study should not lead the reader to believe that a QM/MM model of ligands such as Cp* would always be acceptable in the study of reaction paths. We want to stress the need to closely associate the models selected for representing ligands to the reaction types. A change of oxidation state and coordination number at the metal centre require that the electronic and steric properties of all ligands be properly represented. Full QM modelling of a ligand similar to that in the experimental situation is a conservative safe choice. In the case of a reaction with no change of oxidation state, the electronic properties of the ligand may be of less importance. In the particular case of ions with large radii like lanthanides, the steric bulk of ligands plays an important role. A QM/MM representation of ligands may therefore be appropriate with the additional advantage, especially in the case of lanthanide complexes, of permitting calculations of much larger systems. Regretfully maybe, the time is past where modelling experimental ligands by much smaller isolobal groups was acceptable.

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