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Hydrogen sensitivity – A systematic computational study of electronic effects

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Abstract

Hydrogen sensitivity, defined as the preference of a metal alkyl for hydrogenolysis over olefin insertion, was studied computationally (DFT) for a series of simple model catalysts, including some metallocenes and a few basic models of heterogeneous catalysts. As a measure of electrophilicity, we have used the complexation energy to the probe molecule ammonia. For isolated species in the gas phase, complexation energies appear to dominate the chemistry. Ethene complexes more strongly than hydrogen, and with increasing electrophilicity of the metal centre this difference grows; the hydrogen sensitivity decreases accordingly. This result seems to agree both in broad terms with the experimental lower hydrogen sensitivity of heterogeneous catalysts, and more specifically with the increased hydrogen sensitivity of highly alkylated or fused metallocenes. The opposite conclusion reached by Blom et al. [R. Blom, O. Swang, R.H. Heyn, Macromol. Chem. Phys. 203 (2002) 381] is due to the use of a very different measure of electrophilicity, rather than to different experimental data.

Keywords: Hydrogen sensitivity; Hydrogen response; Metallocenes; Electrophilicity; DFT

1. Introduction

Hydrogen sensitivity is a key parameter of olefin polymerization catalysts. Hydrogen is commonly used as a molecular weight control agent [1]. Single-site catalysts tend to be much more sensitive to hydrogen than heterogeneous Ziegler–Natta catalysts; Phillips-type chromium oxide catalysts have an extremely low hydrogen sensitivity [2]. A high hydrogen sensitivity can not only lead to low molecular weights, but also to low net activity in the presence of hydrogen, since the hydrides formed in the chain termination reaction are highly reactive and can decompose/deactivate much more quickly than the propagating polymeryl species themselves [3]. Also, hydrides show low regioselectivity for α-olefin insertion [4], and secondary alkyls formed by 2,1-insertion in a metal-hydrogen bond may well become ”dormant” [5]. On the other hand, “dormant” species can be re-activated by hydrogen, so that in many other cases addition of hydrogen results in *higher* activity (as well as lower molecular weight) [5]. The wide variation in hydrogen sensitivity of catalytic systems complicates the use of mixtures of catalysts in a single reactor for the deliberate generation of bimodal molecular weight distributions.

The factors governing hydrogen sensitivity are poorly understood and have received little attention from computational chemists. At the most basic level, hydrogen sensitivity can be described as the competition between monomer coordination/insertion and hydrogen coordination/σ-bond metathesis (Scheme 1). In the absence of hydrogen, the main chain termination step is usually chain transfer to monomer, also illustrated in Scheme 1.

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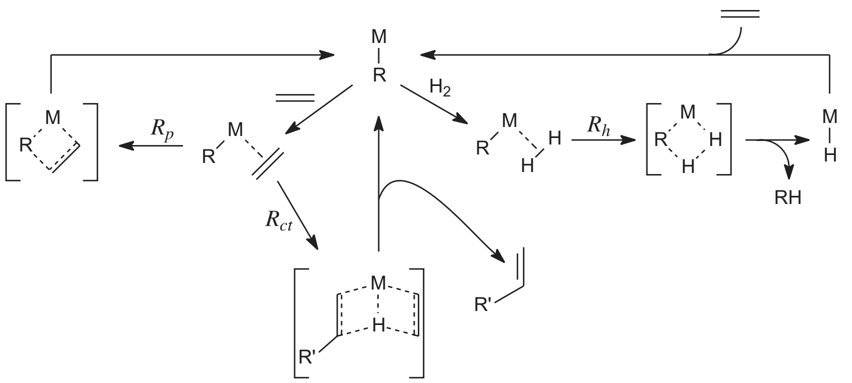


Scheme 1. Competing insertion, chain transfer to monomer, and hydrogenolysis.

The degree of polymerization resulting from these competing reactions is given by the ratio of propagation to all contributing chain termination reactions:

$$P_\mathrm{n} = \frac{R_\mathrm{p}}{\sum R_\mathrm{term}} = \frac{R_\mathrm{p}}{R_\mathrm{ct} + R_\mathrm{h} + \ldots} \tag{1}$$

In industrial applications, R_ct is low and R_h is the dominant chain termination process, so that $P_\mathrm{n} \approx R_\mathrm{p}/R_\mathrm{h}$. The elementary steps of insertion, chain transfer to monomer and hydrogenolysis have been studied computationally in some detail [6,7], but the effect of catalyst variation has only been studied systematically for the propagation and chain transfer to monomer steps [8].

In a gas-phase reactivity study of metallocene alkyl cations, Richardson et al. found a correlation between electrophilicity of the metal centre and ease of hydrogenolysis [9a]. They argued that Ind_2Zr^+ is less electrophilic than Cp_2Zr^+, although recent work by the group of Chirik [10] indicates that the "indenyl effect" in metallocene catalysis is related to the *higher* electrophilicity of the metal centre in Ind_2 complexes, rather than to changes in hapticity that would be possible with indenyls but not with cyclopentadienyls. A correlation with experimental ^{91}Zr chemical shifts and calculated ESP charges for a limited set of metallocene catalysts led Blom et al. [11] to conclude that electrophilicity increases in the order $Cp_2Zr < Ind_2Zr < Cp_2^*Zr$ (a somewhat counterintuitive result), and that hydrogen sensitivity of the polymerization catalysts increases in the same order. In the present work, we examine a wide range of simple model ligands (**a**–**s**, Scheme 2) in order to explore the electronic factors determining hydrogen sensitivity. We compare Ti^{IV}, (**1**) Ti^{III} (**2**) and Zr^{IV} (**3**) in these ligand environments, and try to correlate the predicted hydrogen sensitivity with the Lewis acidity of the metal centre.

The model systems chosen here (except for **l**, **m**, **o** and **p**) are not intended to represent any "real" catalyst. They are far too small and simple for that. Primarily, we want to elucidate the electronic factors underlying hydrogen sensitivity, without having complications due to steric effects. "Real" catalysts are invariably much more crowded, and steric factors must be at least as important as electronic factors there. Indeed, we included a limited set of more realistic systems (**3l**, **3m**, **3o** and **3p**) to allow a direct comparison with the experimental data presented by the groups of Richardson [9] and Blom [11]. However, our focus is on evaluation of electronic effects, which should be useful in the design of new catalysts with tailored hydrogen sensitivity.

2. Methods

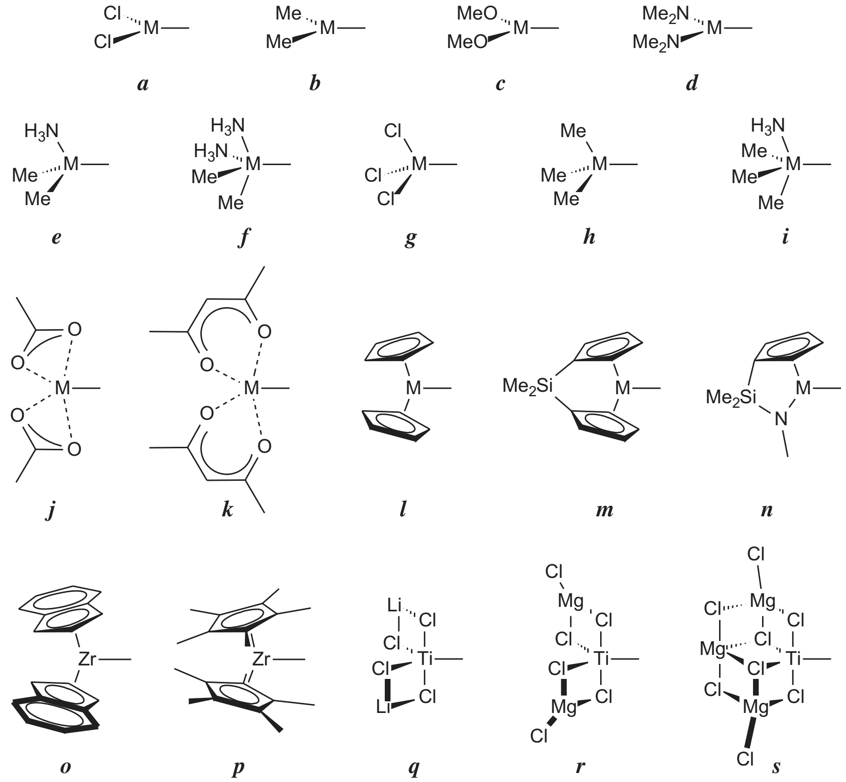
All geometries were optimized as minima or transition states at the restricted (Ti^{IV} and Zr^{IV}) or unrestricted (Ti^{III}) b3-lyp [12]/SV(P) [13] level (small-core pseudopotential for Zr [14]), using the Turbomole program [15] coupled to the Baker optimizer [16]. Stationary points were characterized by vibrational analyses (analytical for closed-shell species, numerical for open-shell species), and thermal corrections (enthalpy and entropy) were calculated at 273 K, 1 bar, using the standard formulae of statistical thermodynamics. Improved single-point electronic energies were calculated at the b3-lyp/TZVPP [17] level, and final free energies were obtained by combining these electronic energies with the SV(P) thermal corrections. No solvent corrections were carried out since (a) the model systems were not intended to directly represent any "real" system and (b) the models are small, resulting in unrealistically high solvent accessibility of the metal centre and hence overestimation of solvent effects.

For Ti^{III} complexes, there often are several electronic states that are close in energy and can be converged separately. The lowest-energy states were obtained by deliberately mixing the α SOMO and LUMO orbitals and then re-converging the wavefunction. This kind of problem is most likely to occur for small, symmetric systems, and will probably be less important for larger, more realistic models.

3. Results and discussion

3.1. Shape of the energy profile

Table 1 contains collected relative free energies of the adducts of species $L_nMMe^{(+)}$ with H_2, C_2H_4, NH_3 and CO, the transition states for ethene insertion and alkyl hydrogenolysis, and the products of these reactions. In a



Scheme 2. Model systems studied. M = Ti^{IV} (1), Ti^{III} (2), Zr^{IV} (3).

number of cases, mostly for neutral systems (see Table 1), the C_2H_4 and H_2 adducts were unstable to ligand dissociation. In a few cases, a complex could be calculated, but it was higher in (electronic) energy than the separated reactants, presumably with a small barrier to dissociation. Even where the electronic energy of the adduct is lower than that of the separated reactants, thermal corrections make many C_2H_4 complexes and nearly all H_2 complexes unstable to dissociation. For the strongest donor NH_3, on the other hand, only complexation to a few neutral species (e.g. **1h**, **1i**, **2k**, **2l**, **3i**) is endergonic. The binding strength of CO is intermediate between these extremes.

Fig. 1 shows some possible energy profiles for the two competing reactions (we are ignoring solvent and counterion effects for the moment). In profile A, typical of highly unsaturated cationic complexes (e.g. **1a**, **3b**), olefin complexation is strong, and insertion occurs at an energy lower than that of the free alkyl. Hydrogen complexation, on the other hand, is rather weak, and hydrogenolysis occurs at an energy well above the free alkyl. Under these conditions, the resting state will be the olefin complex, olefin-hydrogen exchange will be a pre-equilibrium to hydrogenolysis, and the energy difference $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}(H_2)–\Delta G^{\ddagger}(\text{ins})$ determines the hydrogen sensitivity via a Boltzmann expression (*high* $\Delta\Delta G^{\ddagger}$ values corresponding to *low* sensitivity).

One arrives at the same conclusion for systems where both complexation energies are smaller. In the extreme of negligible complexation (B), the uncomplexed metal alkyl becomes the resting state (e.g. **1l**, **3o**), but $\Delta\Delta G^{\ddagger}$ still determines the hydrogen sensitivity. The only situation that would lead to different kinetics would be that of C, where both hydrogen and olefin bind strongly, and both react at energies below that of the free alkyl: once a complex is formed, it will react before it can revert to the free alkyl or exchange hydrogen for olefin. However, we have found no cases where the transition state for hydrogenolysis is lower in free energy than the isolated metal alkyl, so our conclusion is that $\Delta\Delta G^{\ddagger}$ is the correct measure of hydrogen sensitivity for the systems studied here.

3.2. Hydrogen sensitivity and electrophilicity

Table 2 lists the calculated hydrogen sensitivities $\Delta\Delta G^{\ddagger}$ for the various systems studied (*positive* values mean *propagation* is preferred). Highly electrophilic 3-coordinate cationic Ti^{IV} and Zr^{IV} complexes (**a**, **b**) have a very high preference for propagation over hydrogenolysis. Reducing the electrophilicity by adding extra donor atoms, either in the form of additional ligand molecules (**e**, **f**) or by introducing ligands with additional intramolecular donor groups (**j**, **k**) increases the hydrogen sensitivity, as does the introduction of π-donor groups (**c**, **d**). Cyclopentadienyl groups are extremely strong π-donors by comparison, and induce a complete switch to preferred hydrogenolysis.

Neutral Ti^{IV} systems like Me_3TiMe (**1h**) are much less electrophilic than cationic species like $Me_2(NH_3)TiMe^+$ (**1e**) and show a high hydrogen sensitivity. The neutral Ti^{III} complexes do not resemble their cationic Ti^{IV} analogs

Table 1
Free energies (relative to MMe) of various complexes and transition states (kcal/mol)

Metal	System		C_2H_4 complex	Ins TS	M–Pr	H_2 compl	Hydrogen TS	M–H	NH_3 complex	CO complex
Ti^{IV}	Cl_2TiMe^+	**1a**	−23.6	−15.0	−23.3	−3.7	6.2	6.9	−49.4	−17.6
	Me_2TiMe^+	**1b**	−17.9	−7.0	−17.4	−1.2	11.2	2.9	−40.8	−12.3
	$(MeO)_2TiMe^+$	**1c**	−18.8	−6.1	−17.0	−2.1	8.4	−0.2	−39.9	−13.2
	$(Me_2N)_2TiMe^+$	**1d**	−11.7	4.1	−12.5	−0.4	12.1	−2.7	−31.4	−11.4
	$(NH_3)Me_2TiMe^+$	**1e**	10.7	20.3	−6.9	[a]	27.7	0.9	−13.6	6.9
	$(NH_3)_2Me_2TiMe^+$	**1f**	[a]	31.4	−11.0	[a]	29.3	−6.1	−3.2	10.0
	Ac_2TiMe^+	**1j**	3.4	20.3	−10.3	7.3	28.5	4.0	−20.7	2.2
	$Acac_2TiMe^+$	**1k**	[a]	32.8	−5.6	[a]	33.3	−0.4	−1.6	14.5
	Cp_2TiMe^+	**1l**	5.8	14.5	−11.2	6.0	7.1	−12.6	−18.3	−6.8
	$\{Me_2SiCp_2\}TiMe^+$	**1m**	4.7	12.6	−11.8	5.8	6.7	−10.2	−18.4	−7.4
	$\{CpSiMe_2NMe\}TiMe^+$	**1n**	−7.6	3.3	−12.8	1.8	8.8	−1.6	−28.8	−9.2
	$\{Li_2Cl_4\}TiMe^+$	**1q**	17.1	23.5	−6.9	[a]	31.2	−2.3	−6.6	12.8
	$\{Mg_2Cl_6\}TiMe^+$	**1r**	[a]	18.3	−9.3	[a]	30.8	0.9	−12.5	11.3
	$\{Mg_3Cl_8\}TiMe^+$	**1s**	3.1	7.9	−14.2	8.6	17.1	0.6	−24.3	−1.6
	Cl_3TiMe	**1g**	[a]	39.3	−6.5	[a]	35.0	−3.4	0.6	12.7
	Me_3TiMe	**1h**	[a]	41.4	−3.4	[a]	32.7	−3.5	7.1	17.6
	$(NH_3)Me_3TiMe$	**1i**	[a]	43.8	−3.4	[a]	31.6	−9.2	13.1	15.0
Ti^{III}	Cl_2TiMe	**2a**	0.9	19.1	−2.8	11.6	19.7	1.9	−12.6	−1.1
	Me_2TiMe	**2b**	−1.8	20.5	−2.6	11.2	18.6	−4.9	−7.3	−2.9
	$(MeO)_2TiMe$	**2c**	0.0	22.0	−2.1	11.3	18.9	−6.9	−3.5	−3.6
	$(Me_2N)_2TiMe$	**2d**	10.6	24.2	−2.1	11.0	20.6	−8.0	−3.9	−5.3
	$(NH_3)Me_2TiMe$	**2e**	6.0	26.5	−2.4	8.9	23.0	−9.1	−3.9	−1.8
	$(NH_3)_2Me_2TiMe$	**2f**	12.7	29.7	−2.6	12.3	22.3	−12.4	2.9	−1.8
	Ac_2TiMe	**2j**	12.7	29.8	−3.0	[a]	29.2	−4.9	−1.6	5.6
	$Acac_2TiMe$	**2k**	19.3	36.4	−4.1	[a]	30.9	−9.0	4.2	10.5
	Cp_2TiMe	**2l**	19.5	34.9	0.8	13.8	18.5	−14.0	3.8	2.0
	$\{Me_2SiCp_2\}TiMe$	**2m**	18.0	33.6	0.2	13.4	17.9	−11.0	2.6	1.9
	$\{CpSiMe_2NMe\}TiMe$	**2n**	6.1	23.6	−2.3	9.3	18.8	−6.5	−3.4	−1.8
	$\{Li_2Cl_4\}TiMe$	**2q**	[a]	20.2	−3.8	[a]	22.6	−0.8	[b]	0.7
	$\{Mg_2Cl_6\}TiMe$	**2r**	[a]	20.1	−4.4	[a]	25.3	2.1	[b]	2.8
	$\{Mg_3Cl_8\}TiMe$	**2s**	4.4	16.5	−9.0	6.0	19.0	4.2	−15.2	−3.2
Zr^{IV}	Cl_2ZrMe^+	**3a**	−23.1	−10.9	−18.6	−3.1	8.8	4.2	−46.9	−15.5
	Me_2ZrMe^+	**3b**	−16.3	−2.7	−12.5	−1.3	13.7	1.3	−38.6	−11.0
	$(MeO)_2ZrMe^+$	**3c**	−16.2	−1.9	−12.8	−0.6	12.3	−1.7	−37.7	−10.7
	$(Me_2N)_2ZrMe^+$	**3d**	−13.5	4.4	−10.9	−0.6	11.9	−3.9	−32.7	−12.1
	$(NH_3)Me_2ZrMe^+$	**3e**	4.1	14.0	−7.1	[a]	25.1	−1.1	−18.4	1.8
	$(NH_3)_2Me_2ZrMe^+$	**3f**	11.6	28.0	−9.2	[a]	29.0	−4.6	−10.0	6.6
	Ac_2ZrMe^+	**3j**	−3.0	15.9	−9.2	2.7	25.1	1.9	−27.1	−2.9
	$Acac_2ZrMe^+$	**3k**	[a]	28.6	−4.6	[a]	30.8	−2.3	−8.5	8.4
	Cp_2ZrMe^+	**3l**	−3.8	6.3	−13.2	1.2	5.7	−10.1	−26.6	−10.3
	$\{Me_2SiCp_2\}ZrMe^+$	**3m**	−5.7	5.3	−12.5	0.8	5.5	−9.9	−27.2	−9.9
	$\{CpSiMe_2NMe\}ZrMe^+$	**3n**	−11.4	1.5	−10.7	0.5	8.8	−5.2	−31.1	−9.0
	Ind_2ZrMe^+	**3o**	1.0	13.3	−8.9	4.2	10.7	−9.9	−21.9	−6.5
	$Cp^*_2ZrMe^+$	**3p**	9.2	17.4	−3.6	6.5	10.4	−13.2	−16.9	−3.6
	Cl_3ZrMe	**3g**	[a]	34.0	−5.0	[a]	31.7	−3.6	−6.4	7.4
	Me_3ZrMe	**3h**	[a]	36.0	−3.2	[a]	28.3	−4.8	1.5	11.8
	$(NH_3)Me_3ZrMe$	**3i**	[a]	40.8	−3.4	[a]	29.1	−8.4	9.1	14.6

[a] No complex formed, spontaneous dissociation.

[b] Complex splits off a Li–Cl or Mg–Cl fragment on optimization.

much, but instead show a behaviour more similar to that of neutral Ti^{IV} complexes, with a mostly modest (in case of Cp complexes, a pronounced) preference for hydrogenolysis. Notable exceptions here are the "heterogeneous" models **2q**, **2r** and **2s** which still prefer propagation.

While this picture seems to be reasonable, it would be helpful to have a more quantitative measure of electrophilicity to plot against hydrogen sensitivity. To this end, we calculated the complexation energies ΔG_b of all fragments with the strong σ-donor NH_3 and the much weaker donor CO (note that by definition these complexation energies are the *negative* of the relative energies of NH_3 and C_2H_4 complexes as listed in Table 1; the same holds for ΔG_b values used in other figures). Fig. 2 shows that the ethene binding strength is approximately proportional to that of NH_3, though with a slope less than 1.0 (since ethene is obviously a weaker donor). The (significant) deviations for Ti^{III} complexes might be due to the possibility of backdonation from Ti^{III} to C_2H_4 but not to NH_3. Figure S1 shows a similar trend for CO; Figure S2 shows that hydrogen complexa-

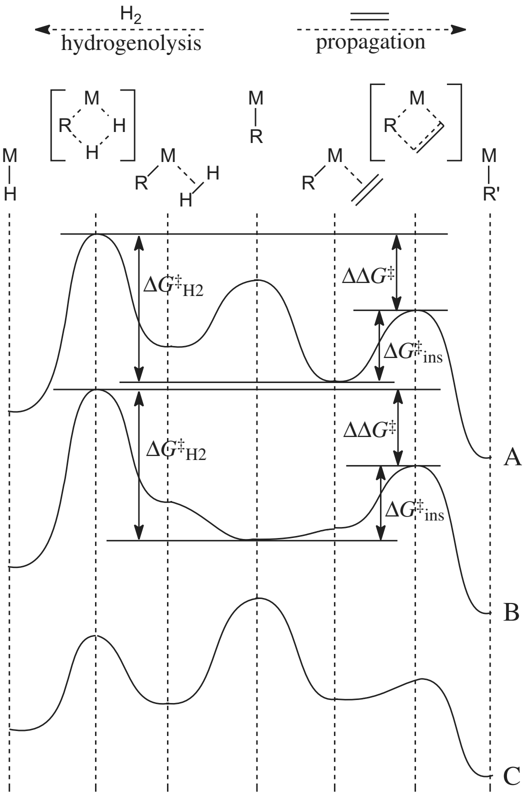


Fig. 1. Alternative free energy profiles for insertion and hydrogenolysis.

tion, while much weaker than that of either C_2H_4 or CO, also follows NH_3 complexation. We conclude that the NH_3 complexation energy is a useful measure of Lewis acidity or electrophilicity.

If we now plot the calculated hydrogen sensitivity $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}(H_2)–\Delta G^{\ddagger}(ins)$ against NH_3 complexation energy, we again find a reasonable correlation (Fig. 3). Gratifyingly, the regions for Ti^{IV}, Ti^{III} and Zr^{IV} overlap considerably, indicating that electrophilicity is the main determinant of hydrogen sensitivity, without any specific influence of either the metal (Ti vs Zr) or oxidation state (Ti^{IV} vs Ti^{III}) [18]. If we would manage to generate comparable Lewis acidity for e.g. a Ti^{IV} and a Ti^{III} complex (obviously by using very different ligand sets for the two systems), we can expect roughly comparable hydrogen sensitivities.

From these results, we tentatively conclude that the electronic preference is controlled by the strength of binding of the incoming reactant (C_2H_4 or H_2). Ethene is the better donor of the two [19], so highly electrophilic systems bind ethene more strongly than H_2. Once the reactant is bound, the barrier for the subsequent reaction is relatively low, so everything is dominated by the complexation energy. For the less electrophilic systems, the complexation energies are smaller, and so are the differences between them.

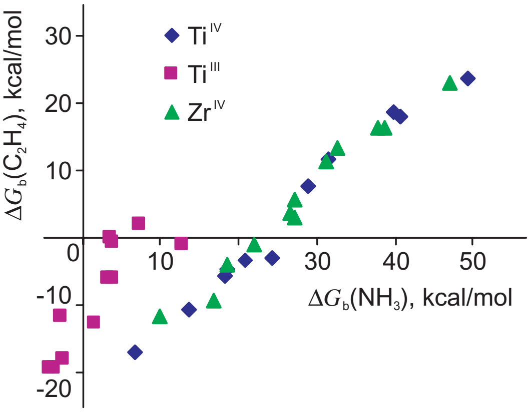


Fig. 2. Correlation between calculated complexation energies of NH_3 and C_2H_4.

Table 2
Calculated hydrogen sensitivity $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}$ $(H_2)–\Delta G^{\ddagger}$ (ins) (kcal/mol)

System		Ti^{IV}, **1**	Ti^{III}, **2**	Zr^{IV}, **3**
Cl_2MMe	**a**	20.8	−4.8	19.4
Me_2MMe	**b**	17.8	−6.7	16.0
$(MeO)_2MMe$	**c**	14.1	−3.5	13.9
$(Me_2N)_2MMe$	**d**	7.6	−4.0	7.2
$(NH_3)Me_2MMe$	**e**	7.0	−4.0	10.7
$(NH_3)_2Me_2MMe$	**f**	−2.5	−7.8	0.6
Ac_2MMe	**j**	7.8	−1.0	8.8
$Acac_2MMe$	**k**	0.2	−5.9	1.8
Cp_2MMe	**l**	−7.8	−16.8	−1.0
$\{Me_2SiCp_2\}MMe$	**m**	−6.3	−16.1	−0.1
$\{CpSiMe_2NMe\}MMe$	**n**	5.1	−5.3	6.9
Ind_2MMe	**o**			−3.0
Cp^{*}_2MMe	**p**			−7.4
$\{Li_2Cl_4\}TiMe$	**q**	7.2	2.0	n/a
$\{Mg_2Cl_6\}TiMe$	**r**	12.1	4.8	n/a
$\{Mg_3Cl_8\}TiMe$	**s**	8.8	2.1	n/a
Cl_3MMe	**g**	−4.6	n/a	−2.7
Me_3MMe	**h**	−9.0	n/a	−8.1
$(NH_3)Me_3MMe$	**i**	−12.5	n/a	−12.1

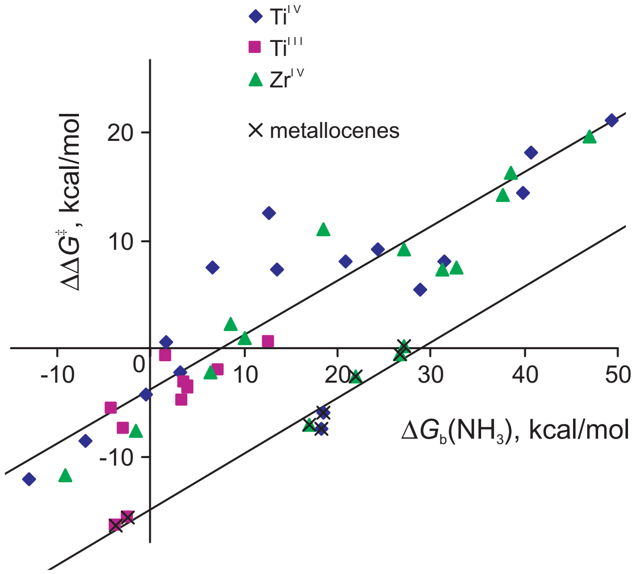


Fig. 3. Hydrogen sensitivity as a function of metal electrophilicity. The lines shown have been calculated separately for the metallocene and non-metallocene data in the graph.

3.3. The case of metallocenes

Metallocenes appear to deviate most from the trend mentioned above. They have fairly large NH_3 complexation energies, comparable to, e.g. the analogous carboxylates, yet their hydrogen sensitivity is much higher (they are the eight points most below the general trend in Fig. 3). We believe that this is at least partly a steric effect. The metallocenes are rather crowded close to the metal centre. This does not hinder the approach of H_2 much, and even favours the elongation of the M–C bond that occurs at the transition state. However, the close approach of the olefin needed for both complexation and insertion is more hindered. The effect on the difference in *reaction energies* is revealing in this respect: hydrogenolysis is more exothermic for the metallocenes than for any other species considered.

If we consider the metallocenes as a group, their hydrogen sensitivities are shifted by ca. 10 kcal/mol from the trend seen with the other systems, but seem to follow a parallel line: hydrogen sensitivity still *decreases* with increasing electrophilicity. At first sight, these data seem to contradict the conclusions of both Richardson et al. and Blom et al. However, there is no contradiction with the *experimental* results reported by the group of Blom [11]. They find that hydrogen sensitivity increases in the order $Cp_2Zr < Ind_2Zr < Cp_2^*Zr$, just as we predict on the basis of the calculations. Even in a quantitative sense, there seems to be a reasonable agreement [11c], considering that counterion and solvent have been neglected in the calculations. Rather, the different conclusion reached by Blom et al. is due to a different choice of measure of electrophilicity. These authors concluded from ^{91}Zr chemical shifts and calculated charges that Cp_2^*Zr is more electrophilic than Cp_2Zr, whereas our calculated NH_3 complexation energies seem to indicate the opposite. Unfortunately, electrophilicity is not a well-defined concept corresponding to a unique physical observable, so the choice of measure of electrophilicity is largely one of taste and personal preference. However, when faced with two measures indicating diametrically opposite trends, we believe that choosing the one directly connected with ligand binding strength corresponds best to the intuition of organometallic chemists. With this choice of measure, electrophilicity *increases* in the order Cp_2^*Zr (**3p**) < Ind_2Zr (**3o**) < Cp_2Zr (**3l**) < Me_2Si-Cp_2Zr (**3m**) < $\{CpSiMe_2, NMe\}Zr$ (**3n**), while hydrogen sensitivity *decreases* in this order.

One has to be cautious not to over-interpret the agreement between theory and experiment regarding electrophilicity and hydrogen sensitivity. For the case of ethene polymerization, in particular, it is possible that the rate-limiting step of propagation does not correspond to the actual insertion step but rather to e.g. anion displacement [20] or chain re-orientation [21]. In that case, the agreement we find could be largely fortuitous. On the other hand, we have argued before that for olefins other than ethene, insertion itself is more likely to be the rate-limiting step in propagation [21a]. It follows that for such olefins one might be more confident of finding the trend we predict, i.e. an increase in hydrogen sensitivity for less electrophilic systems.

One might expect that a comparison with the work by the group of Richardson [9] would be more straightforward, because now both experimental and computational data are for isolated gas-phase cations. However, we are using free-energy values to predict preference, and these are only valid under conditions of fast thermalization and Boltzmann energy distributions. In Richardson's gas-phase experiments, the isolated cations are first thermalized, but then they collide with a substrate molecule and react (or dissociate again) before the collision and complexation energy has been dissipated. Thus, the observed rates, while valid in themselves, are for species with a non-Boltzmann energy distribution, and for an average internal energy different for each system [9c], and so cannot be directly correlated with free-energy values at any specific temperature.

Richardson's data seem to imply that hydrogen sensitivity *increases* with increasing electrophilicity, although the error margins in the k_{H_2}/k_p values are quite high. In view of the above-mentioned difficulty in correlating gas-phase results with calculated data, we refrain from speculation about this apparent discrepancy. Still, the computational results indicate that, in agreement with observations by Richardson et al., both insertion and hydrogenolysis taken separately become faster for more electrophilic systems. Fig. 4 illustrates the hydrogenolysis case. The position of the metallocene data is again noticeable: they lie below the main body of the data points, implying that hydrogenolysis is abnormally easy for this class of compounds.

In 1992, Richardson et al. used ligand effects on electron-transfer equilibria between substituted ruthenocenes to define a parameter γ describing the "electronic ligand effect" of cyclopentadienyl-like ligands [22]. The scale for γ is anchored to 0.0 for the unsubstituted cyclopentadienyl group, and to -1.0 for the more electron-donating Cp^* group; strongly electron-withdrawing ligands have positive γ values (e.g. $C_5H(CF_3)_4$, 3.10). In later studies of gas-phase chemistry, reactivity of metallocene cations was found to follow trends in $\sum\gamma$ (sum of γ parameters for the ligands attached to the metal), indicating that this

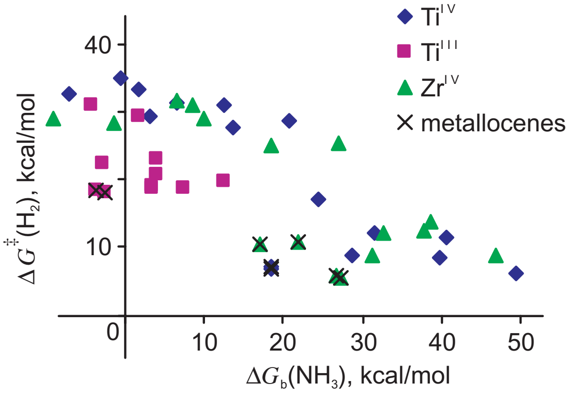


Fig. 4. Free energy of activation for hydrogenolysis (relative to M–Me complex) vs ammonia complexation energy (kcal/mol).

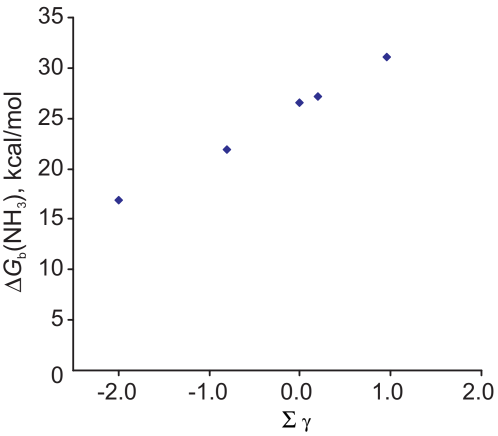


Fig. 5. Correlation between Richardson's γ parameter and calculated ammonia complexation energy.

can be used as a measure of electrophilicity of substituted metallocenium cations [9]. Thus, it seems useful to compare this measure with our calculated complexation energy of the probe molecule ammonia. The ammonia complexation values calculated for Zr complexes follow the same trend as these γ values, with electrophilicity decreasing in the order **3n** > **3m** > **3l** > **3o** > **3p**. Even quantitatively, the correlation appears to be good (Fig. 5), suggesting that both are useful measures of "electrophilicity".

4. Conclusions

Our calculations indicate that in principle hydrogen sensitivity, defined as the preference for hydrogenolysis over propagation, should show a clear *inverse* correlation with electrophilicity of the metal centre. This trend is interpreted in terms of the dominant effect of complex formation on the energy profile. Although many factors (like catalyst dormancy and deactivation issues) complicate the comparison with experiment, this seems to agree with experimental data, both in broad terms (relatively high sensitivity of single-site catalysts compared to traditional Ziegler–Natta and Phillips catalysts [2]) and within the metallocene series [11]. Metallocenes as a class seem to be more sensitive to hydrogen than expected on the basis of electrophilicity alone, which we tentatively ascribe to steric effects. Nevertheless, calculations suggest that within their class they follow the same trend.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.030.

References

[1] (a) L.L. Böhm, Polymer 19 (1978) 562;
(b) E. Albizzati, U. Gionnini, G. Collina, L. Noristi, L. Resconi, Catalysts and Polymerizations, in: E.P. Moore (Ed.), Polypropylene Handbook, Carl Hanser Verlag, Munich, 1996, p. 76 (Chapter 2).

[2] (a) W. Kaminsky, H. Lüker, Makromol. Chem. Rapid Commun. 5 (1984) 225;
(b) See e.g., W.A. Fraser, C.C. Williams, W.H. Sachs, Manufacturing efficiencies from metallocene catalysis in gas-phase polyethylene production <http://www.univation.com/technotes/metallocene.pdf>;
(c) Union Carbide chromocene-based catalysts have a much higher hydrogen sensitivity than chromium oxide Phillips catalysts, but are still less sensitive than single-site catalysts.

[3] E. Albizzati, M. Galimberti, U. Giannini, G. Morini, Macromol. Chem. Symp 48/49 (1991) 23.

[4] J.C. Chadwick, Macromol. Symp. 173 (2001) 21.

[5] (a) J.C. Chadwick, A. Miedema, O. Sudholter, Makromol. Chem. 195 (1994) 167;
(b) V. Busico, R. Cipullo, P. Corradini, Makromol. Chem. Rapid Commun. 13 (1992) 15;
(c) T. Tsutsui, N. Kashiwa, A. Mizuno, Makromol. Chem. Rapid Commun. 11 (1990) 565.

[6] (a) T.K. Woo, L. Fan, T. Ziegler, Organometallics 13 (1994) 432;
(b) T. Yoshida, N. Koga, K. Morokuma, Organometallics 14 (1995) 746.

[7] (a) Y.A. Ustynyuk, L.Y. Ustynyuk, D.N. Laikov, V.V. Lunin, J. Organomet. Chem. 597 (2000) 182;
(b) L. Petitjean, D. Pattou, M.F. Ruiz-López, Tetrahedron 57 (2001) 2769.

[8] (a) P. Margl, L. Deng, T. Ziegler, Organometallics 17 (1998) 933;
(b) P. Margl, L. Deng, T. Ziegler, J. Am. Chem. Soc. 120 (1998) 5517;
(c) P. Margl, L. Deng, T. Ziegler, J. Am. Chem. Soc. 121 (1999) 154;
(d) R. Schmid, T. Ziegler, Organometallics 19 (2000) 2756.

[9] (a) N.G. Alameddin, M.F. Ryan, J.R. Eyler, A.R. Siedle, D.E. Richardson, Organometallics 14 (1995) 5005;
(b) D.E. Richardson, N.G. Alameddin, M.F. Ryan, T. Hayes, J.R. Eyler, A.R. Siedle, J. Am. Chem. Soc. 118 (1996) 11244;
(c) The olefin or H_2 complexation energy, which becomes available as internal energy on complex formation, will be different for each different cation/substrate combination.

[10] C.A. Bradley, I. Keresztes, E. Lobkovsky, P.J. Chirik, Organometallics 25 (2006) 2080.

[11] (a) R. Blom, O. Swang, R.H. Heyn, Macromol. Chem. Phys. 203 (2002) 381;
(b) A. Anderson, R. Blom, I.M. Dahl, Macromol. Chem. Phys. 202 (2001) 726;
(c) Estimated for $\Delta\Delta G^{\ddagger}$ (80 °C; kcal/mol) from (a) and (b): 0.2 (Cp_2Zr), −2.2 (Ind_2Zr), −2.6 (Cp_2^*Zr); calculated from the DFT results: −1.5, −3.8, −8.4.

[12] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
(b) A.D. Becke, J. Chem. Phys. 98 (1993) 1372;
(c) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(d) All calculations were performed using the Turbomole functional "b3-lyp", which is not identical to the Gaussian "B3LYP" functional.

[13] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.

[14] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123.

[15] (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165;
(b) O. Treutler, R. Ahlrichs, J. Chem. Phys. 102 (1995) 346;
(c) R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, C. Hättig, H. Horn, C. Huber, U. Huniar, M. Kattannek, A. Köhn, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, K. Tsereteli, B. Unterreiner, M. von Arnim, F. Weigend, P. Weis, H. Weiss, Turbomole Version 5, January 2002, Theoretical Chemistry Group, University of Karlsruhe.

[16] (a) PQS version 2.4, 2001. Parallel Quantum Solutions, Fayetteville, Arkansas, USA (the Baker optimizer is available separately from PQS upon request);
(b) J. Baker, J. Comput. Chem. 7 (1986) 385.

[17] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.

[18] The points for Ti^{III} in Fig. 3 do not seem to deviate as much from the general trend as in Fig. 2, which suggests that the effects of backdonation from Ti^{III} on the two reactions being compared cancel.

[19] The relative energies in Table 1, which show ethene binding to be endergonic in most cases, are somewhat misleading. The electronic binding energy is significant for most cationic complexes, but the entropy term causes the mostly positive relative free energy values. Note that a positive relative free energy of $MMe(C_2H_4)$ relative to MMe species corresponds to a negative ethene binding energy.

[20] (a) Z. Xu, K. Vanka, T. Ziegler, Organometallics 23 (2004) 104;
(b) G. Lanza, I.L. Fragala, T.J. Marks, Organometallics 21 (2002) 5594.

[21] (a) N. Friederichs, B. Wang, P.H.M. Budzelaar, B.B. Coussens, J. Mol. Catal. A 242 (2005) 91;
(b) J.C.W. Lohrenz, T.K. Woo, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 12793.

[22] M.F. Ryan, A.R. Siedle, M.J. Burk, D.E. Richardson, Organometallics 11 (1992) 4231.