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Reduction of chromium in ethylene polymerisation using bis(imido)chromium(VI) catalyst precursors†

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Hybrid density functional calculations on $[Cr(NR)_2C_3H_7(C_2H_4)]^+$ (R = H, ^tBu) have revealed a facile reductive elimination reaction involving β-hydrogen transfer from the alkyl chain, suggesting that the active species in ethylene polymerisation with bis(imido)chromium(VI) precursors contains a reduced chromium atom.

The technical importance of polymer materials having novel structures and properties has in recent years resulted in the development of a number of new classes of catalyst for the polymerisation of olefins.[1] One interesting design strategy involves the application of dianionic ligands for which an isolobal[2] relationship with the monoanionic cyclopentadienyl moiety can be drawn. Using bis(organoimido) ligands Gibson *et al.*[3,4] have synthesised isolobal group V and VI analogues of the group IV metallocenes which, in the presence of standard activators or in the form of well-defined alkyl cations, have proved catalytically active for the polymerisation of ethylene. The bis(imido)chromium catalysts appear to be robust sustaining polymerisation activity for several hours.[4] The dihalides and dialkyls furthermore tolerate the presence of functional groups, allowing the polymerisation of acrylonitrile[5] and the cyclopropanation of unsaturated esters.[6]

In a recent theoretical investigation of the role of bis(imido)chromium–alkyl cations, we found migratory insertion of ethylene into the Cr–alkyl bond to be less facile than that in corresponding studies of group IV based catalysts, as a result of the higher barrier to inversion around the metal centre in the Cr(VI) compounds.[7] In contrast, the addition of ethylene to the Cr=N double bond proceeds with a very low barrier suggesting that the resulting azachromacycle could be a starting point for further modification of the Cr(VI) cations.

We have now investigated the reactivity of the azachromacyclobutane species using hybrid density functional theory§ and report here on a facile route to reduction of the Cr(VI) centre which suggests that the active species of the bis(imido)chromium catalysts involve chromium atoms having a lower oxidation state.

Using a propyl fragment as the starting polymer chain,¶ we have explored reactions of ethylene with the alkyl chromium(VI) cations $[Cr(NR)_2C_3H_7]^+$,‖ initially with hydrogen as the substituent on the nitrogen atoms (R = H). Ethylene complexation to the apex of such a three-coordinate cation (*i.e.* frontside coordination) has been found to be energetically favourable and to proceed without a barrier.[7] The free energies given in Fig. 1 suggest that the resulting π complex, **1Fβ**,** is the resting state of propagation at this (assumed) active centre. The propagation may proceed directly from the frontside complex to form a γ-agostic product, **2γ**, or *via* an inversion at the metal centre to form a backside complex before ethylene inserts to form a δ-agostic product.[7] Backside coordination of ethylene is practically blocked[7] and insertion from this position requires a frontside-to-backside rearrangement. The rearrange-

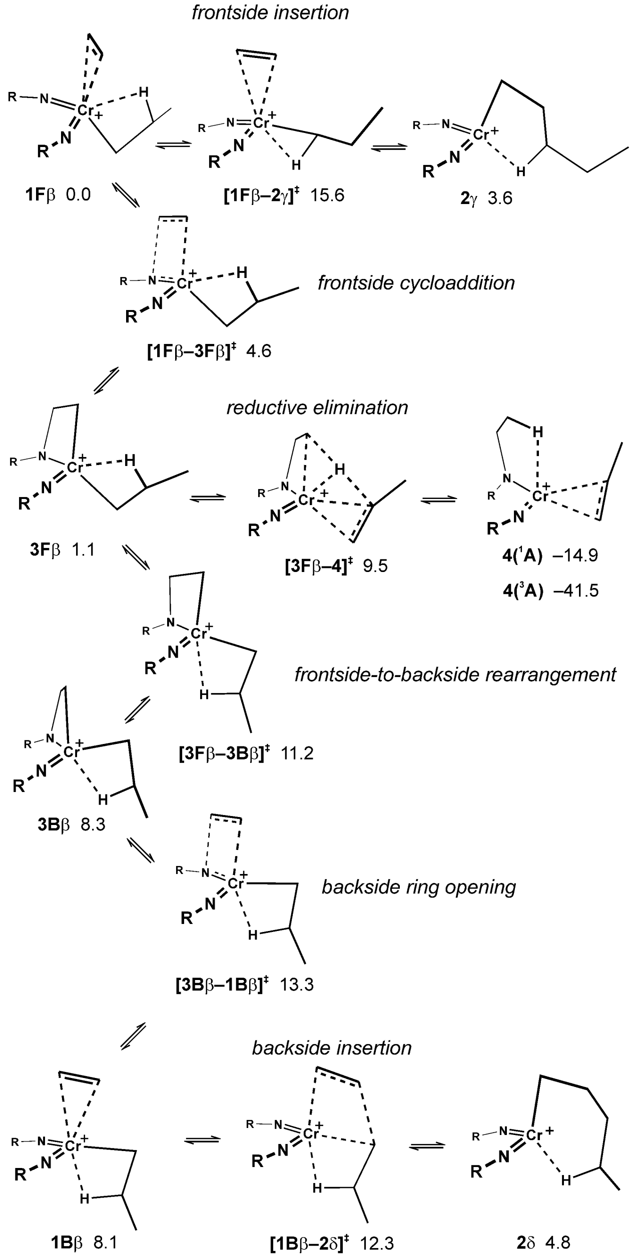

Fig. 1 Stationary points along the reaction paths of ethylene insertion and chromium reduction in $[Cr(NR)_2C_3H_7(C_2H_4)]^+$. The structures shown are those actually optimised for R = H. Gibbs free energies (kcal mol^{-1}) at 25 °C pertaining to R = H are given relative to the frontside π complex, **1Fβ**, which has 13.4 kcal mol^{-1} lower free energy than the separated reactants, $[Cr(NR)_2C_3H_7]^+$ and C_2H_4.

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† Electronic supplementary information available: Cartesian coordinate files of the computed stationary points. See http://www.rsc.org/suppdata/cc/b1/b110296f/

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Table 1 Calculated energies given relative to the resting state, **1F**β[a]

	R = H		R = ^{t}Bu	
Species[b]	ΔH_{298}	ΔG_{298}	ΔH_{298}	ΔG_{298}
[**1F**β–**2**γ]‡	14.2	15.6	13.8	15.5
3Fβ	−0.7	1.1	3.5	6.4
[**3F**β–**4**]‡	6.9	9.5	13.6	16.7
[**3B**β–**1B**β]‡	10.7	13.3	14.0	17.0
[**1B**β–**2**δ]‡	9.7	12.3	10.8	13.6

[a] In kcal mol^{-1}. [b] See Fig. 1 for labelling.

ment is preferably performed starting from the β-agostic azachromacyclobutane [2 + 2] addition product, **3F**β, and is completed by recoordination of the β-agostic hydrogen atom through the base of the N$_2$Cr–propyl pyramid.†† However, **3F**β is also the starting point of a facile β-hydrogen transfer from the growing chain to the azachromacycle (transition state [**3F**β–**4**]§), thereby forming an α-olefin coordinating to the chromium(IV) metal atom in a highly exothermic reductive elimination reaction. If we assume that spin-flipping to reach the triplet state is not a bottleneck, then the reduction can be considered to be practically irreversible. The number of organometallic reactions reported to involve more than one spin state is growing rapidly;[8] a recent example involves homogeneous chromium-based ethylene oligomerisation.[9]

Since the fate of the alkyl chromium(VI) cation is determined by the rate of the above described propagation and termination reactions, the relevant stationary points have also been investigated for the system involving a ^{t}Bu-substituted imido ligand (R = ^{t}Bu) as a more realistic model. The hydrogen transfer reaction involves a seven-membered cyclic transition state which is destabilised by steric bulk. Backside opening of the azachromacyclobutane ring (**3B**β–**1B**β) is also hindered by the sterically demanding ^{t}Bu groups. Thus, for the realistic alkyl chromium cation, the barriers of all three competing reactions (two propagations and one reduction) are calculated to have comparable values (see Table 1). It is at present not possible to rank the barriers further. Tests indicate, however, that the calculated relative stabilities of the involved transition states are only weakly dependent on the method applied.‡‡ Furthermore, because the reduction appears to be irreversible, the Cr(VI) cations may be reduced rapidly after exposure to ethylene even if the corresponding reaction rate were to be a few orders of magnitude lower than that of insertion.

Sustained polymerisation activity over several hours[4] could thus be explained by an active centre involving a reduced chromium atom rather than Cr(VI). The nature of this reduced active species has not yet been investigated and we do not exclude further reduction or other modifications of **4**. There is considerable evidence suggesting that both Cr(III)[10] and Cr(IV)[11] species are capable of mediating the ethylene polymerisation reaction. The occurrence of reductive elimination in six-valent chromium alkyls to reach one of these intermediate oxidation states would not be surprising: For the chromium-based Phillips catalyst,[12] it is well established that while the calcined catalyst displays chromium in oxidation state VI,[12] inlet of ethylene leads to the reduction of chromium under evolution of formaldehyde.[13]

Since our investigation has been concerned with the migratory insertion mechanism only, we cannot exclude a different Cr(VI)-mediated propagation reaction with a significantly lower barrier to activation than that calculated here. Nevertheless, such a result would also serve to underline the difference between the high-valent titanium and chromium alkyls in spite of their isolobal relationship.

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Notes and references

§ Geometries, frequencies and thermochemical quantities were computed using the Gaussian implementation[14] of Becke's three-parameter hybrid density functional method (B3LYP) as detailed previously.[7] We used a valence-triple-ζ basis set for chromium and valence double-ζ basis sets for second-row and hydrogen atoms. Polarisation functions were added to carbon atoms being part of the ethylene or the polymer chain as well as to nitrogen. All energies reported in the current work are based on single-point B3LYP energy calculations using basis sets that were improved compared to those used during geometry optimisations: all N, C and H atoms were described by augmented Dunning triple-ζ sets (TZD2P)[15] to account for known basis set sensitivities.[15]

¶ The catalyst precursors are usually dibenzyl derivatives. The Cr–benzyl species, however, is only relevant to the initiating species.[4,7]

‖ The catalytically active sites are thought to involve cationic alkyl species of chromium.[4] In modelling these cationic species, effects from counter ion and solvent have been neglected. It appears, however, that at least solvent effects would tend to strengthen our conclusions based on the present ionic catalyst model.[7]

** Intermediates are labelled by Arabic numerals (**1**–**4**) and, in the case of ethylene π complexes or the related products of ethylene addition to the Cr=N double bond, by capital **F** or **B** to indicate whether the complex can be considered 'frontside' or 'backside',[7] respectively. For agostic Cr–H–C structures, Greek letters are used to identify the carbon atom involved. For the two spin states of the product of reduction, the molecular term symbol (^{3}A or ^{1}A) is added. Transition states are identified by a bracket enclosing the product and the reactant separated by a dash and followed by the suffix '‡'.

†† Recoordination of the β-agostic H atom induces a practically planar N$_2$Cr–propyl configuration and is rate-determining in the frontside-to-backside rearrangement. The initial stages of this reaction (decoordination of the frontside agostic H atom and rotation through ~ 180° about the Cr–propyl bond) involve significantly lower barriers.

‡‡ Based on single-point energy calculations using a pure non-local density functional (BPW91, as implemented and described in ref. 14), the free-energy barriers to frontside insertion, (**1F**β–**2**γ), and reduction, (**3F**β–**4**), for the R = ^{t}Bu system, are reduced by 0.3 and 3.4 kcal mol^{-1}, respectively, as compared to the corresponding entries in Table 1.

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