

Reactivity of Chromium Complexes under Spin Control

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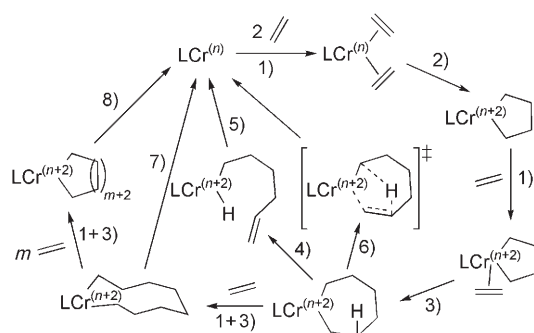
arene ligands · bridging ligands · chromium ·
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Over the last few years, many chromium complexes have been found to catalyze the selective trimerization and tetramerization of olefins, a transformation achieved by only a few other metals.^[1] For example, catalysts with very high activity and selectivity for the production of 1-hexene or 1-octene have been developed, with an associated industrial plant in operation since 2003. The unique selectivity is commonly attributed to a metallacyclic mechanism with reductive elimination and oxidative coupling steps, as shown in Scheme 1. A similar metallacyclic mechanism may also be

mechanism can also afford a route to polymerization with increasing ring size (8). Deuterium labeling studies give convincing evidence for such a metallacyclic mechanism for both trimerization^[4] and polymerization.^[5] A homogeneous trimerization catalyst has been shown to produce some polyethylene with an end-group distribution similar to the industrial Phillips polymer.^[6] Thus, the mechanism of polymerization and trimerization are probably closely linked.

Although the general metallacyclic mechanism is widely accepted—at least for the selective trimerization—many important mechanistic details remain unclear. The two oxidation states of chromium have been proposed as I/III or II/IV.^[1] The reductive elimination may occur by the β -H elimination to an alkyl-hydride complex (4) followed by reductive C–H elimination (5) or by a direct hydride transfer to the other chromium alkyl group (6). In addition, the activity and selectivity depends significantly on the anion, cocatalyst, or other additives (halide effect).^[7] Recent computational work has supported the idea that interactions with these external reagents during olefin insertion into the metallacycle (3) and/or during the reductive elimination (5–8) can alter the activation barriers.^[8] Although a monometallic mechanism is generally assumed, analogous bimetallic mechanisms based on two chromium(II) sites can also be formulated.^[9]

Attempts have been made to determine the oxidation states during catalysis by experimental and computational studies. Magnetic-moment measurements using the Evans method for different catalysts were consistent with the oxidation states II, III, or IV in the resting state, although large errors associated with this method warrant some caution.^[10] Although chromium(II) complexes have been isolated from chromium(III) precursors under catalytic conditions, recent results suggest that chromium(III) rather than chromium(II) is responsible for the selectivity.^[11] It has also been shown that chromium(III) complexes can be formed under catalytic conditions even when starting from a chromium(II) precursor.^[12] Recent results by Bercaw and co-workers have further shown that chromium(III) dialkyl/diaryl complexes lead directly to the catalytic trimerization.^[13] New studies on these complexes with nitrogen-bridged diphosphine ligands (PNP donor ligands) have extended the range of substrates to dienes which allow a C–C reductive elimination to cyclic products as well.^[14] Density-functional calculations with the assumption of no change in spin state give viable routes for both the $\text{Cr}^{\text{II/IV}}$ ($S=1$) and $\text{Cr}^{\text{I/III}}$ ($S=3/2$) catalytic cycles.^[15] However, a change in spin state between the



Scheme 1. Metallacyclic olefin oligomerization: olefin coordination (1), oxidative coupling (2), olefin insertion (3), β -H elimination (4) followed by reductive C–H elimination (5) or reductive elimination by concerted H transfer (6) giving a trimer, tetramer (7), or oligo/polymer (8).

in operation for the Phillips catalyst—one of the most important for industrial ethylene polymerization.^[2] This heterogeneous catalyst, based on silica-supported chromium oxide, is unique as it does not require a cocatalyst to be active and it produces a polymer with butyl side chains without adding 1-hexene.^[3] The oxidative coupling of ethylene at a reduced chromium species as in Scheme 1 (2) would explain the alkyl-free initiation and partial ethylene trimerization leading to hexene formation followed by incorporation into the polymer to give butyl side chains. A metallacyclic

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oxidation states is possible and may even accelerate the reaction step if a spin flip is sufficiently fast.^[16] Computational studies on such spin-forbidden reactions are much more difficult. Substantial progress has recently been made but not yet extended to the reaction steps in Scheme 1.^[17] Thus, additional experimental evidence is needed for assessing whether the fundamental steps in Scheme 1 can also proceed under spin change.

The reductive C–H elimination step (5) is believed to be facile if the reaction product is a stable complex, and especially when the hydride and alkyl group are in close proximity. Most kinetic studies have shown that the olefin insertion steps (1–3) are rate limiting and not the reductive elimination (5–8).^[11] Theopold and co-workers have recently reported the crystal structures of two bi-metallic chromium complexes that appear to be the direct precursor **1** and product **2** of a reductive C–H elimination (Figure 1).^[18]

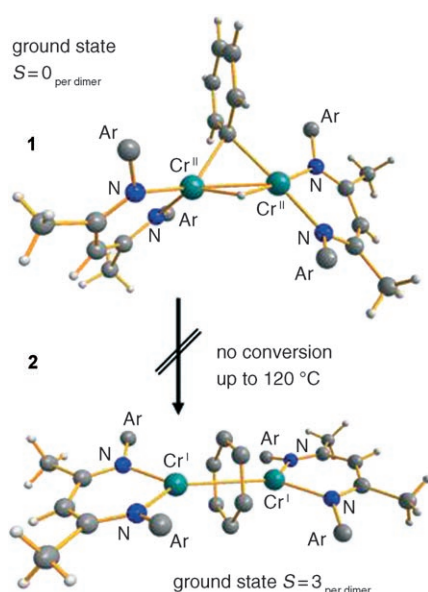


Figure 1. Structures of the hypothetical starting complex **1** and the hypothetical product of reductive C–H elimination **2** (Ar = *o,o*-*i*Pr₂-(C₆H₃)).^[18]

Complex **1** contains a bridging hydride and bridging phenyl ligand between two Cr^{II} centers in a *cis* position, with a C_{ipso}⋯H distance of only 2.57 Å and a C_{ipso}–Cr–H angle of 80°. Thus, all structural features are ideally set up for a reductive elimination. The structure of **2** is very similar to that of **1**, except that the phenyl–hydride is now a η⁶–η⁶-bridging benzene between two Cr^I centers. The distance between the two chromium atoms increases from 2.63 to 3.52 Å, but the Cr–N bonds to the ketimine ligands remain similar to within 0.01 Å. Thus, complex **2** represents the product of the hypothetical reductive C–H elimination of **1** including the eliminated benzene as a probably very stable η⁶-arene complex to chromium(I). However, complex **1** is stable to elimination for extended periods of time at up to 120 °C and complex **2** cannot be detected as a decomposition product. Instead, complex **2** was prepared by the magnesium reduction

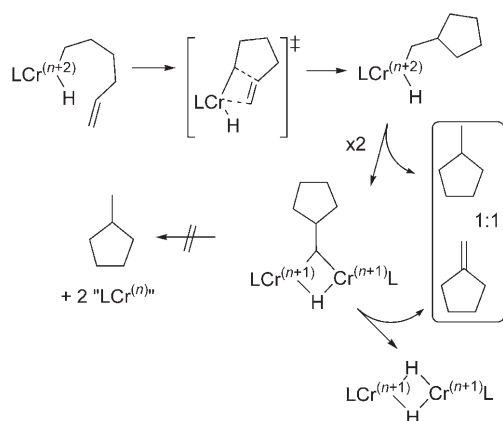
of [(Ar₂nacnac)Cr^{II}Cl]₂ (Ar₂nacnac = ArNC(Me)CHC(Me)NAr) in the presence of benzene as a thermally stable compound (up to 80 °C) without any evidence of **1** being formed at higher temperature. Thus, while both complexes are thermally stable, they cannot be interconverted. An analogous chromium(II) alkyl hydride complex has previously been found to be similarly stable towards reductive elimination.^[19]

A possible reason for this lack of interconversion was revealed by magnetic susceptibility studies. Complex **1** has an *S* = 0 ground state with thermally accessible low energy paramagnetic excited states leading to a room temperature magnetic moment of 2.4 μ_B with strong antiferromagnetic coupling between the chromium centers. On the other hand, complex **2** has an *S* = 3 ground state with strong ferromagnetic coupling between two chromium(I) centers having three unpaired electrons each. Therefore, the lack of reductive elimination from **1** to **2** provides a dramatic case of “spin blocking”—an otherwise facile reaction completely inhibited by incompatible spin states between reactant and product.

It is also interesting to note the unusual spin state of **2**. Each chromium center (d⁵) is neither low spin (*S* = 1/2) nor high spin (*S* = 5/2) but an intermediate *S* = 3/2 state possible only for non-axially symmetric complexes.^[20] This spin state would make chromium(I) complexes spin-compatible with the commonly found chromium(III) (d³) complexes with the same spin state. This leads to the interesting speculation that an important role of the ancillary ligand in catalysts for the selective olefin trimerization is the stabilization of the reduced chromium(I) center in this intermediate *S* = 3/2 spin state for fast oxidative coupling and reductive elimination steps. The complex **2** is in fact a binuclear, neutral version of the triazacyclohexane chromium(I) arene intermediate we postulated for selective α-olefin trimerization catalysts.^[10] An *S* = 3/2 ground state was calculated for a similar complex, [CpCr^I(ethene)₃].^[15b] Thus, a Cr^I/Cr^{III} catalytic cycle can remain in one spin state and would be a viable alternative to the proposed Cr^{II}/Cr^{IV} cycle.

One intriguing side reaction in the selective oligomerization of ethylene is the formation of equal amounts of methylcyclopentane and methylenecyclopentane as the major byproducts in the C₆ fraction. A mechanistic study of this side reaction has led to a proposal of a binuclear alkyl–hydride bridged species of intermediate oxidation state (i.e. Cr^{II} for a cycle based on Cr^{III}) (Scheme 2).^[21] Key to this mechanism is the proposed inability of the binuclear complex to undergo reductive C–H elimination. The isolation of the stable aryl–hydride complex **1** and the stable product **2** without interconversion supports this assumption. The observation of these cyclic side products and the slow alkyl–hydride elimination suggest that the direct path (Scheme 1, (6)) is dominating and leads to the trimerization product while a minor path (4) leads to the cyclic by-products.

In a recent development, the catalytic cycle of chromium complexes with PNP donor ligands has also been accessed from chromium(I) carbonyl complexes after decarbonylation with AlEt₃, further supporting the Cr^I/Cr^{III} cycle.^[22] Only the spin state of the chromium(I) carbonyl complex of *S* = 1/2 has been determined—but the spin state of the decarbonylated



Scheme 2. Binuclear mechanism proposed for the formation of cyclic by-products in the observed 1:1 ratio. Reductive C–H elimination would only lead to saturated side-products.^[21]

catalytic species may well be $S = \frac{3}{2}$ based on the apparent importance of the spin state for the redox cycle.

In summary, great progress has been made in understanding reactions involved in the catalytic olefin trimerization and tetramerization based on chromium. The high reactivity of some systems and the lack of expected reactivity of others owing to “spin-blocking” highlight the importance of the spin states of all intermediates. In particular the reductive C–H elimination—a key step in the catalytic cycle—can be completely suppressed when the spin states are not compatible. Future computational studies on these systems will also have to consider challenging spin-forbidden reaction pathways to understand the reactivity.

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