Homogeneous Chromium Catalysts for Olefin Polymerization

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Chromium-based heterogeneous catalysts are used extensively for the polymerization of olefins. There are few homogeneous model systems that allow investigation of the reaction mechanisms and unique characteristics of chromium catalysts. Coordinatively unsaturated paramagnetic chromium alkyls containing a $Cp^*Cr^{III}R$ fragment ($Cp^* = \eta^5\text{-}C_5Me_5$, pentamethylcyclopentadienyl) catalyze the polymerization of ethylene and α-olefins. Correlations between molecular structure and catalytic activity are reviewed.

Introduction

Polymers produced by homopolymerization and/or copolymerization of small olefins such as ethylene and propene are among the most widely used plastics. In 1996 worldwide consumption of polyethylene and polypropylene stood at 40×10^6 and 21×10^6 tons, respectively.[1] Except for so-called low density polyethylene (LDPE), which is made by a high temperature/high pressure radical process, these materials are the products of metal-catalyzed reactions conducted on an enormous scale. Two different kinds of catalysts are used commercially . One group utilizes group 4 metals (Ti, Zr) and can be traced to the Nobel prize-winning discoveries of Ziegler and Natta.[2] There has been much recent interest in this area, due to the development and application of so-called "metallocene" technology, i.e. catalysts based on sophisticated organometallic molecules that facilitate greater control of polymer structure and properties.[3] The second kind of catalyst is based on chromium and was discovered independently by Hogan and Banks at Phillips Petroleum Co.[4] Roughly one third of all polyethylene is currently produced with it, and it is notable for not requiring any cocatalyst (e.g. AlR_3 or methyl aluminoxane, i.e. MAO). Despite much investigative effort, much less is known about the mechanism and active site(s) of this catalyst, and it has not undergone innovations to match the "metallocene revolution". A large obstacle in this regard has been the lack of homogeneous model systems for chromium-based heterogeneous catalysts. This is now beginning to change, and this review covers the relevant organometallic chemistry of chromium, with particular emphasis on studies carried out in the author's laboratory.

The Phillips catalyst is prepared by impregnation of silica with an inorganic chromium compound (e.g. CrO_3 or various Cr^{III} salts), followed by calcination in oxygen.[5] This leaves the chromium in the hexavalent state. Upon contact with ethylene, the metal is reduced, ultimately forming the catalytically active species. With carbon monoxide as an alternative reducing agent, the surface-bound chromium

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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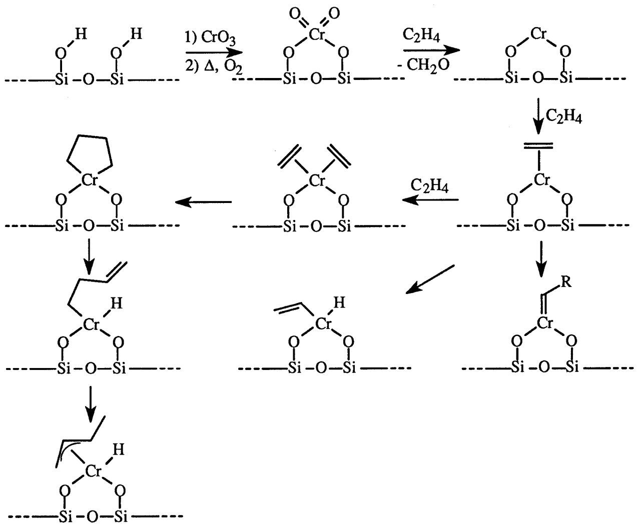
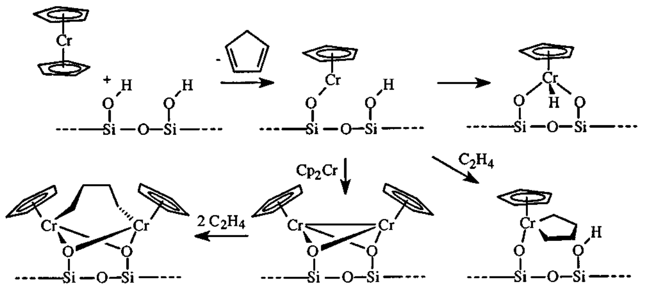
can be reduced to its divalent state (Cr^{II}), and this species will polymerize ethylene.[6] However, the chemical structure, valence state, and mechanism of formation of the active site, i.e. the chromium alkyl actually producing the polymer by repetitive insertion of ethylene, have been the subject of a longstanding controversy. Especially the valence (i.e. the formal oxidation state) of the catalytically active chromium has inspired much speculation, and almost every stable oxidation state of chromium has been held responsible for catalysis at one time or another. Scheme 1 depicts some of the proposed structures; several of the organometallic derivatives could in principle undergo ethylene insertion. Variations of these structures containing binuclear chromium sites (with and without metal−metal bonds) have also been proposed.

Scheme 1



Another chromium catalyst was discovered by Karapinka[7a] and developed by Karol et al.[7b] at Union Carbide in the early 60's. It is prepared by impregnating dehydroxylated silica with chromocene (Cp$_2$Cr, Cp = η^5-cyclopentadienyl). While not in use industrially at present, the Union Carbide catalyst shares some of the advantages of the Phillips catalyst, namely high activity and absence of cocatalyst. It is different from the latter, however, in its high selectivity between ethylene and propene (no copolymerization) and its good response to hydrogen (H$_2$) for molecular weight control. There is little doubt that the reaction of the organometallic molecule with remaining hydroxyl groups on the silica surface results in loss of one cyclopentadienyl ligand and formation of a surface bound CpCr fragment (see Scheme 2). However, it is also clear that the remaining cyclopentadienyl group does not initiate the polymer chain growth; rather it stays coordinated to the chromium during catalysis. Thus there arises the same set of questions about the mechanism of the initiation, and the structure and valence of the active site. Scheme 2 shows some of the commonly proposed candidates for the active site.

Scheme 2



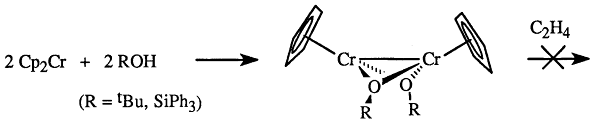
Homogeneous Model Systems

The proposed structures depicted in Schemes 1 and 2 have resulted from many spectroscopic investigations of heterogeneous catalysts combined with extrapolations from the now extensive body of known organometallic structures. However, the relevance of this "deluge of conjecture"[8] is highly questionable. Most of the analytical work utilized IR spectroscopy[9], with some EXAFS[10] and solid state ^{1}H NMR[11] results added relatively recently. Even for pure substances, most of these techniques can hardly be called definitive structural tools, and synthetic organometallic chemists would not base a detailed molecular structure solely on such results. Furthermore, the most careful studies of this type have come to the conclusion that the catalytically active sites represent only a very small fraction of the surface-bound chromium (< 1%!).[9b] Thus, whatever spectroscopic information is available probably pertains to those chromium species that are inactive. The proposals were further compromised by the fact that until recently the organometallic chemistry of chromium—i.e. the very metal of concern—did not offer realistic model compounds for any of the suggested species. As we have previously noted, "the known organometallic chemistry of said metal concerns low-valent carbonyl derivatives and/or diamagnetic complexes with 18-electron configurations. Such molecules are unlikely candidates for modeling highly reactive (coordinatively unsaturated) and oxide supported alkylchromium compounds".[12] This lacuna in the development of molecular chromium chemistry is largely due to the physical properties of relevant compounds. Chromium alkyls in the intermediate oxidation states of interest (II−IV) are typically "metallaradicals" featuring unpaired electrons. The associated paramagnetism makes characterization by NMR spectroscopy, the most important analytical tool of solution chemistry, more difficult and less informative.[13]

Nevertheless, we are convinced that homogeneous organometallic chemistry is in a position to make an important contribution both to the understanding of present-day heterogeneous catalysts and to the development of the next generation of chromium catalysts. To this end we must create functional models, i.e. well-defined chromium compounds that catalyze the polymerization of olefins in homogeneous solution. The preparation and catalytic activity of molecules incorporating the structural elements of Schemes 1 and 2 will be the best arbiter of their relevance. If a structurally characterized Cr^{IV} metallacycle, to name but one example, does not polymerize ethylene in solution (see below), it is unlikely to do so on a silica surface. Conversely, if a class of coordinatively unsaturated CpCr^{III} alkyls consistently exhibits catalytic activity, it must have some claim to being related to the catalytically active site of the Union Carbide catalyst. Let us then review the available homogeneous chemistry.

Cyclopentadienyl Chromium Catalysts

The Union Carbide catalyst is prepared by treatment of silica with chromocene. There have, of course, been attempts to model this reaction with surface hydroxyl groups in homogeneous solution by reaction of chromocene with alcohols or silanols.[14] The products of such reactions are invariably dinuclear Cr^{II} alkoxides (see eq. 1); they do not polymerize or even react with ethylene. One of the obvious advantages of surface-supported organometallics is "site-isolation", i.e. the inability of coordinatively unsaturated species to dimerize and thereby annihilate reaction sites. With respect to the initiation of catalysis, an investigation of the reactivity of a mononuclear complex of the type CpCr^{II}−OR would be desirable; however, such a molecule has not been prepared. The closest we have come is the synthesis of mononuclear Tp^{tBu,Me}Cr−OPh [Tp^{tBu,Me} = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borato]; the sterically hindered tris(pyrazolyl)borate ligand is isoelectronic to the Cp ring, but its steric bulk prevents dimerization.[15] However, Tp^{tBu,Me}Cr−OPh does not react with ethylene.

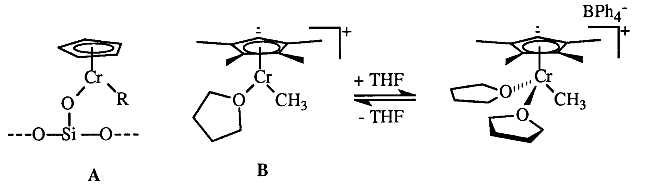


(1)

Chromocene by itself does not catalyze the polymerization of ethylene. However, in the presence of an excess of aluminum alkyl and at high ethylene pressure some polymer has been obtained. Under the same conditions, a variety of chromium π-complexes [including bis(arene)chromium$^{0/+}$, CpCr(acac)Br, and CpCr(NO)$_2$X] showed some activity.[16] Wilke et al. found that hexane solutions of tris(allyl)chromium polymerize ethylene under mild conditions[17]; although not a cylopentadienyl derivative, Cr(η^3-C$_3$H$_5$)$_3$ is chemically related to Cp$_2$Cr. The structure of the mixed ligand system CpCr(η^3- C$_3$H$_5$)$_2$ has been reported; its reaction with ethylene has not been described in the literature[18], but it is said to be active at modest ethylene pressure.[18c] Bis(indenyl)chromium, a dimeric complex featuring bridging μ-η^3-indenyl ligands, is also a catalyst for ethylene polymerization.[19]

The generally accepted mechanism of polymer chain growth involves coordination of ethylene to a metal atom carrying an alkyl functionality, followed by migratory insertion of the olefin into the metal−carbon bond, thereby increasing the length of the alkyl chain by two carbons (Cossee mechanism).[20] Thus a minimum requirement for the active site is an alkyl group (or hydride) bonded to chromium. Keeping in mind the presence of the ancillary Cp ligand, and maintaining the link to the silica surface via an oxygen atom, one might suggest structure **A** (Scheme 3) as an active site of the Union Carbide catalyst.

Scheme 3



Based on this simple proposal, we began some time ago to explore the synthesis and reactivity of cyclopentadienyl chromium alkyls in the +III oxidation state.[21] For all the familiar reasons (e.g. solubility, stability) we opted for preparing the Cp* derivatives (Cp* = η^5-C$_5$Me$_5$, i.e. pentamethylcyclopentadienyl), but the qualitative differences caused by this substitution are expected to be minor.[22] Our first success was the synthesis and structural characterization of [Cp*Cr(THF)$_2$Me]BPh$_4$ (THF = tetrahydrofuran).[12][23] In solution, this paramagnetic 15-electron cation exists in equilibrium with coordinatively unsaturated [Cp*Cr(THF)Me]$^+$, via dissociation of a THF ligand (shown by ^{1}H NMR). Despite their electron deficiency (i.e. three electrons short of the 18-electron configuration), we consider three-legged piano stool complexes of the type Cp*CrLX$_2$[24] "coordinatively saturated". If one considers the cyclopentadienyl ring (Cp*), a tridentate chelating ligand, to be occupying one trigonal face of an octahedron, then three additional ligands suffice to complete the octahedral coordination environment of the Cr^{III} ion, one of the most stable entities known to coordination chemists. We suggest that the 13-electron species (**B** in Scheme 3) is a good structural model of the proposed active site of the heterogeneous catalyst (i. e. **A**). Its positive charge may serve to discourage dimerization of the unsaturated species by electrostatic repulsion.

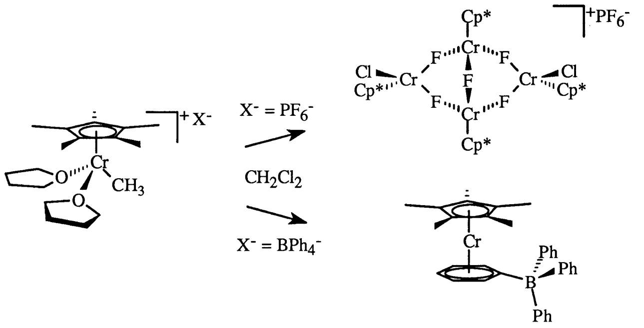
Solutions of [Cp*Cr(THF)$_2$Me]BPh$_4$ in dichloromethane catalyzed the polymerization of ethylene at ambient temperature and pressure, without any added cocatalyst. Attempts to polymerize propene with [Cp*Cr(THF)$_2$Me]BPh$_4$ were unsuccessful, however. In a typical experiment ca. 10 mg of the chromium compound dissolved in 50 ml CH$_2$Cl$_2$ ([cat] = 0.81 mM) produced 1−2 g of polyethylene before activity ceased. Ethylene uptake measurements showed an immediate onset of reaction upon addition of the catalyst. Although no induction period was observed, a slight increase in activity was noted during the initial phase of the reaction. At later times the catalytic activity slowly diminished and effectively ended after ca. one hour. In accord with the dissociation equilibrium depicted in Scheme 3, addition of external THF markedly inhibited the rate of polymerization, presumably by shifting the equilibrium to the coordinatively saturated, unreactive [Cp*Cr(THF)$_2$Me]$^+$ cation. This interpretation was also supported by the observation that analogous complexes with more strongly bonded ligands, e.g. [Cp*Cr(Py)$_2$Et]PF$_6$ (py = pyridine), were much less effective catalysts. ^{1}H NMR experiments and measurements of the rate of polymerization in the presence of various concentrations of THF were used to establish the equilibrium constant for the ligand dissociation [K_{diss} = 1.0(2) M in CH_2Cl_2 at 19°C]. Based on this value, ca 60% of the chromium catalyst exists in the form of the catalytically active 13-electron species $[Cp^*Cr(THF)Me]^+$ under the conditions of the catalytic runs. Taking this into account, the maximum activity measured in these experiments was 1.1 turnover/sec or $>10^5$ g_{PE} $(mol_{Cr}\ h\ atm)^{-1}$, a value that is within an order of magnitude of the quoted activity of commercial catalysts. Measurements of the temperature dependence of the polymerization rate yielded an activation energy (E_a) of 8(1) kcal/mol, which also compares favorably with the value measured for Cp_2Cr/SiO_2 (E_a = 10.1 kcal/mol).[25]

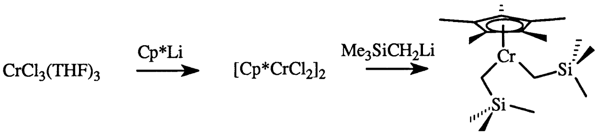
The polymers so obtained were identified as high density polyethylene (HDPE) by IR spectroscopy and melting points (135−140°C). Molecular weight determinations by gel permeation chromatography (GPC) revealed relatively low molecular weights (M_w: 22000−77000; M_n: 14000−20000) and narrow molecular weight distributions (M_w/M_n: 1.9−4.6). The polymers are highly linear, showing no detectable sidebranches by ^{13}C NMR.

The eventual deactivation of the catalysts may be due to several factors. As noted above, the polymerization experiments were carried out without the addition of any cocatalysts. One of the benefits of the latter (typically aluminum alkyls) is their tendency to scrub the ethylene feed of detrimental impurities (e.g. H_2O, O_2), which may react with the catalyst. Without this protection the chromium alkyl will eventually be destroyed. Another possibility may be bimolecular deactivation pathways. β-Hydrogen elimination of a growing polymer chain would yield a Cr^{III} hydride. While such a species might start a new polymer chain (i.e. effect chain transfer) when fixed on a heterogeneous support, we have not been able to prepare a stable mononuclear hydride complex which might model such an intermediate. Attemps to do so have invariably led to reduction to Cr^{II}, presumably accompanied by formation of H_2.[26] Thus β-hydrogen elimination, followed by a binuclear reductive elimination of H_2, may seal the fate of the homogeneous catalyst. A third possibility involves irreversible reactions of the highly electrophilic chromium cation with the solvent or its counterion. In this vein, we have isolated and structurally characterized some unusual chromium complexes resulting from the metal attacking "innocent" anions (see Scheme 4).[12][27] Better noninteracting anions are now available,[28] but only the use of neutral catalysts completely circumvents these problems.

As part of a survey of the factors which are important for the activity of chromium catalysts, it was of interest to ascertain whether the cationic nature of the system described above is essential to the catalysis. After all, its charge is one of the subtle ways model complex **B** differs from the proposed active site **A** (see Scheme 3), which is envisioned as a neutral species. To this end we prepared the neutral dialkyl $Cp^*Cr(CH_2SiMe_3)_2$ (see eq. 2).[29] Although its crystal structure has not been determined yet, the magnetic behavior of the complex in the solid state is consistent with a mononuclear structure devoid of any metal-metal interactions. The effective magnetic moment of $Cp^*Cr(CH_2SiMe_3)_2$ is temperature independent and has a value of μ_{eff} = 3.9(1) μ_B, i.e. the expected spin-only moment for an isolated Cr^{III} ion.

Scheme 4

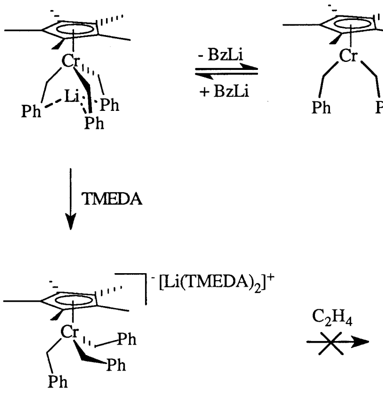




(2)

The steric bulk of the trimethylsilylmethyl groups apparently suffices to prevent dimerization, in contrast to the situation for smaller alkyl groups (see below). There is no spectroscopic evidence for an agostic[30] Cr···H···C interaction, and thus $Cp^*Cr(CH_2SiMe_3)_2$ is best described as a coordinatively unsaturated 13-electron complex. It is also a very good catalyst for the polymerization of ethylene. Hydrocarbon solutions (pentane, toluene) rapidly precipitated polyethylene at reaction temperatures ranging from 0 to −42°C [$Cp^*Cr(CH_2SiMe_3)_2$ slowly decomposes at room temperature]. The polymers had similar physical properties to those produced by $[Cp^*Cr(THF)_2Me]BPh_4$ (M_w: 20000−143000; M_n: 6000−20000; M_w/M_n 3.0−7.0). It is apparent that catalytic activity does not require the chromium alkyl to be positively charged. Indeed, we have found that even an anionic complex can serve as a catalyst precursor. Thus, the ate complex $Li[Cp^*Cr(CH_2Ph)_3]$ (see Scheme 5) polymerized ethylene.[13g] Its rate of polymerization was inhibited by addition of external benzyl lithium, however; presumably dissociation of $LiCH_2Ph$ from the complex generated coordinatively unsaturated $Cp^*Cr(CH_2Ph)_2$, a neutral complex much like $Cp^*Cr(CH_2SiMe_3)_2$. It is probably this intermediate which is responsible for the catalytic activity. Blocking the dissociative pathway, e.g. by sequestering the lithium ion with tetramethylethylenediamine (TMEDA), yielded a coordinatively saturated trialkyl complex, which did not show any polymerization activity. It is not known whether an anionic and yet coordinatively unsaturated Cp^*Cr^{III} alkyl might be active; to test this notion would require the use of a dianionic ligand {e.g. X^{2-} in $[Cp^*Cr^{III}(X)R]^-$}. Even if such a hypothetical 15-electron complex were available, it would still differ in an important way from $[Cp^*Cr(L)R]^+$ and Cp^*CrR_2, both of which exhibit 13-electron configurations. We have not pursued this question.

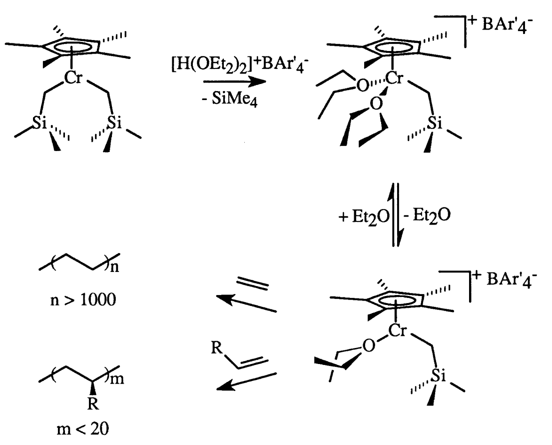
Scheme 5



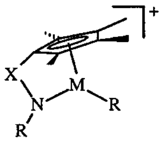
One of the characteristics of the Union Carbide catalyst (Cp_2Cr/SiO_2) distinguishing it from the Phillips catalysts is its pronounced selectivity between ethylene and higher olefins. Basically, it does not react with α-olefins and does not catalyze homopolymerization of the latter or even copolymerization of ethylene with α-olefins. The random incorporation of alkyl branches into the polymer chain gives rise to so-called "linear low density polyethylene" (LLDPE), a material of increasing commercial importance. Our model system seems to behave similarly in this respect as well. It has already been noted that $[Cp^*Cr(THF)_2Me]BPh_4$ failed to polymerize propene under mild conditions. In an attempt to facilitate reaction with α-olefins, and reasoning that the selectivity might be steric in origin, we have prepared chromium complexes with extremely labile ligands. While propene might not be able to compete effectively with THF for the empty coordination site of $[Cp^*Cr(THF)Me]^+$, it might be able to do so if the THF was replaced by a much weaker ligand. With this in mind, we have prepared chromium alkyls stabilized by dialkyl ethers, i.e. $[Cp^*Cr(OR_2)_2CH_2SiMe_3]BAr'_4$ [R = Me, Et, ^{i}Pr; Ar′ = 3,5-bis(trifluoromethyl)phenyl, see Scheme 6].[31] As an indication of the weakness of the chromium−ether bond, structurally characterized $[Cp^*Cr(OEt_2)_2CH_2SiMe_3]BAr'_4$ lost one equivalent of Et_2O when nitrogen gas was passed over the solid. It was also an extremely reactive catalyst, polymerizing ethylene even below its boiling point (b.p. −104°C).

$[Cp^*Cr(OEt_2)_2CH_2SiMe_3]BAr'_4$ also catalyzed the polymerization (or more appropriately, oligomerization) of α-olefins. Reactions of $[Cp^*Cr(OEt_2)_2CH_2SiMe_3]BAr'_4$ with propene and 1-hexene occurred at temperatures close to 0°C and yielded oily residues, which were analyzed by ^1H NMR and GC-MS. They were mixtures of oligomers with degrees of polymerization below 20. Finally, copolymerization experiments, in which the same catalyst was exposed to mixtures of ethylene and an α-olefin, yielded pure polyethylene without any indication (^{13}C NMR) of branching.

Scheme 6



Because of the great interest in copolymerizations, we have made another attempt to tune the reactivity of chromium catalysts in that direction. So-called "constrained geometry" catalysts containing titanium are known to facilitate incorporation of large amounts of α-olefins into a copolymer.[32] The common structural element of these catalysts is an amido group covalently linked to the cyclopentadienyl ligand via a short bridge (1 or 2 atoms) as shown below.[33]

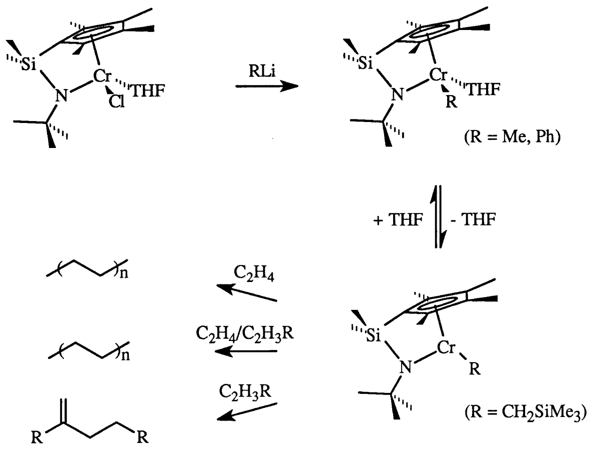


M = Ti, Zr, Hf
X = SiR_2, C_2H_4, etc.

The open access to the metal alkyl is thought to be responsible for the lack of selectivity between different olefins. Hoping to capitalize on this effect, we have prepared isostructural chromium compounds.[34] Scheme 7 shows some of the molecules we have prepared and their reactions with olefins. The sterically demanding trimethylsilylmethyl ligand facilitated the isolation of $[\eta^5\text{-}(Me_4C_5)SiMe_2(N^tBu)]CrCH_2SiMe_3$, i.e. a coordinatively unsaturated Cr^{III} alkyl that has been structurally characterized. True to our expectations, this complex catalyzed the polymerization of ethylene. Remarkably, when the polymerization was carried out in 1-hexene instead of toluene as the solvent, the resulting polymer was still pure polyethylene without any indication of incorporation of the α-olefin. Finally, when the catalyst was presented with pure α-olefin (propene, hexene), a much slower reaction yielded the products of catalytic head-to-tail dimerization and isomerization of the olefin. In this system too, chromium exhibits significant selectivity, favoring ethylene by a wide margin over any other olefin.

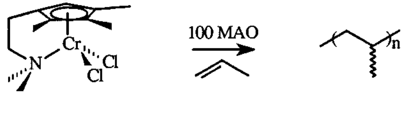
We conclude that the Cp^*Cr^{III} model system exhibits considerable selectivity for ethylene, much like Cp_2Cr/SiO_2. While it possesses some activity for the polymerization/oligomerization of α-olefins, the relative rates of polymerization make copolymerizations impractical. Our observations suggest that several factors limit the polymerization of α-olefins. First, the large difference in temperature at which the reactions commence (i.e. differences in rates) suggests that, for example, either the binding or the insertion

Scheme 7



step greatly favors ethylene over propene. On the other hand, the production of α-olefin oligomers of relatively low molecular weight (including dimers for the "constrained geometry" chromium catalyst) indicates that β-hydrogen elimination of a growing chain is much more facile for a Cp*Cr alkyl with tertiary hydrogen atoms. Whatever the underlying reasons for these preferences, they would appear to make cyclopentadienyl chromium systems unsuitable for α-olefin polymerization.

In this context it is appropriate, however, to mention some ambiguity in the available evidence. Jolly has recently reported that amino-substituted cyclopentadienyl chromium derivatives (see eq. 3), in the presence of methylaluminoxane (MAO:Cr = 100:1), polymerize propene (to atactic polypropylene) and copolymerize ethylene and norbornene to an alternating copolymer.[35] MAO is known to confer remarkable enhancements upon the catalytic activity of group 4 metallocene catalysts, and these observations may suggest that chromium systems will show a similar response. In keeping with the noted lack of cocatalyst requirements of heterogeneous chromium catalysts, we have not explored the effects of MAO on the Cp*Cr system. Conversely, based on our work with closely related compounds, a dialkyl or cationic monoalkyl containing the amino-substituted ligand shown in eq. 3 would not by itself be expected to polymerize propene effectively. This apparent ambiguity awaits further study.



(3)

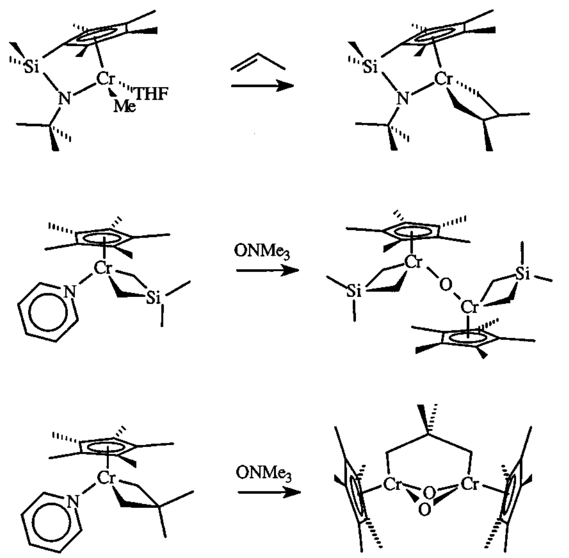
We conclude that *coordinatively unsaturated* Cp^*Cr^{III} alkyls provide a credible structural as well as a functional model for the active site of the Union Carbide catalyst. Their reactivity characteristics parallel those of the heterogeneous catalyst. While the exact origin of the alkyl group in the latter remains unclear, the weight of the available evidence suggests that structure **A** of Scheme 3 is a good approximation of the chromium site in the act of chain propagation. Further support for this notion was provided by a recent theoretical study inspired by $[Cp^*Cr(THF)_2Me]BPh_4$; its authors noted that the Cr^{III} system "displays many similarities to corresponding group IV systems".[36]

As noted in the introduction (see Scheme 3) many other types of organometallic structures have been proposed to account for the activity of the Union Carbide catalyst. Chief among these are various metallacycles, binuclear catalytic sites, and chromium compounds in formal oxidation states other than +III. During our wide-ranging exploration of the organometallic chemistry of Cp*-ligated chromium we have encountered many molecules which may serve as homogeneous models for such species. For the first time, their catalytic competency can thus be tested directly. If a particular structure does not exhibit any catalytic activity or reactivity with ethylene in homogeneous solution, simply grafting it onto a silica surface will not render it catalytically active. Attachment of a catalyst to a solid support has many advantages, but it is not a license for suspending sound chemical reasoning. Naturally, lack of catalytic activity is merely a negative datapoint, and it can always be argued that a model compound does not capture the actual species in detail. However, since we have described a fully functioning model system (see above), proponents of alternative structures now face the challenge of demonstrating that their candidates can actually do the job.

The proposal of a metallacycle is obviously connected to the desire to create an alkyl ligand via a precedented reaction of a metal site with ethylene. Reductive coupling of two ethylene units to a 1,4-butanediyl ligand is such a transformation, and accordingly metallacyclopentanes and dimetallacyclohexanes have often been considered as initiators of chain growth. Assuming, for the sake of the argument, that the lowest accessible oxidation state of chromium in Cp_2Cr/SiO_2 is +II, then coupling of two ethylene molecules on a mononuclear site would generate a Cr^{IV} metallacycle. This relatively rare oxidation state could be circumvented by considering cooperativity of two chromium sites, resulting in a dinuclear metallacycle with two Cr^{III} centers (see Scheme 2). Other, more complicated sequences of events are conceivable and might lead to any combination of ring size, nuclearity, and oxidation state. In any case, Scheme 8 shows some structurally characterized chromium metallacycles prepared as part of our studies.[37]

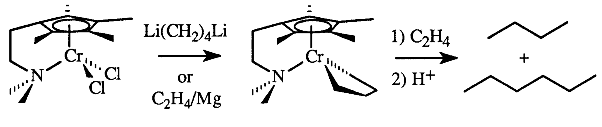
Most of these contain four-membered rings; however, it is unlikely that the slight difference in ring size would affect the insertion of ethylene. While the exact mechanism of formation of these molecules has not been determined in all cases, it seems probable that the Cr^{IV} metallacyclopentane with the "constrained geometry" ligand is the product of a reductive coupling of propene, i.e. the very reaction envisioned above for the formation of such structures. Its lack of any further reactivity with ethylene is thus all the more disappointing, if not entirely surprising. Indeed, none of the metallacycles depicted in Scheme 8 catalyzed the polymerization of ethylene. The most likely explanation for this lack or reactivity is the fact that all of the molecules are coordinatively saturated, i.e. in addition to the Cp* ligand they

Scheme 8



contain three ligands bonded to chromium. Interestingly, this objection was raised, and promptly dismissed, by one of the champions of a metallacycle intermediate.[9e] In any case, these observations certainly do not support the initiation of the catalysis via a metallacycle.

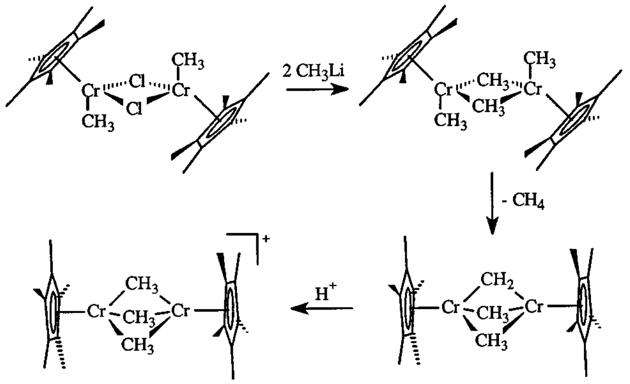
On the same topic, Jolly has reported the preparation of Cr^{III} metallacyclopentanes, inter alia by reductive coupling of ethylene (see eq. 4).[35] These react slowly with ethylene, and the work provides support for the intermediacy of such species in the chromium-catalyzed trimerization of ethylene to hexene.[38] However, activity for the polymerization of ethylene was noted only in the presence of an excess of MAO (100 equiv.). Under these conditions the fate of the metallacycle fragment is unclear.



(4)

Dinuclear chromium sites have often been suggested as the locus of catalytic activity. This may seem somewhat counterintuitive, as metal−metal bonding would be possible under these circumstances, which tends to attenuate the reactivity of metal complexes. The latter expectation seemed to be borne out by our experience with dinuclear chromium alkyls. For example, Scheme 9 shows a sequence of transformations of dinuclear complexes beginning with the synthesis of $[Cp^*(CH_3)Cr(\mu\text{-}CH_3)]_2$.[39] This complex is formally analogous to the catalytically active $Cp^*Cr(CH_2SiMe_3)_2$ (see eq. 2), but the lesser steric hindrance of the methyl groups and the electron deficiency of the metal result in dimerization via bridging alkyl groups. We have analyzed the extent of metal−metal bonding between the pseudooctahedral Cr^{III} atoms.[40] Their structures (d_{Cr-Cr}: 2.4−2.6 Å) and magnetic properties were consistent with some metal−metal interactions, which were also supported by EHMO calculations. Metal−metal bonding is rather unusual in Cr^{III} chemistry, and the interactions must certainly be weak. We noted that addition of even weak ligands (e.g. dissolution in THF) rapidly cleaved both $[Cp^*(CH_3)Cr(\mu\text{-}CH_3)]_2$ [to two equiv. of $Cp^*Cr(THF)(CH_3)_2$] and $[Cp^*_2Cr_2(\mu\text{-}CH_3)_3]^+$ {to $Cp^*Cr(THF)(CH_3)_2$ and $[Cp^*Cr(THF)_2CH_3]^+$}. Apparently the interaction with the cyclic ether is stronger than the Cr−Cr bond. However, ethylene binding was apparently not competitive. None of the molecules depicted in Scheme 9 exhibited any activity for the polymerization of ethylene under mild conditions. Thus we see no compelling advantage in postulating binuclear active sites.

Scheme 9



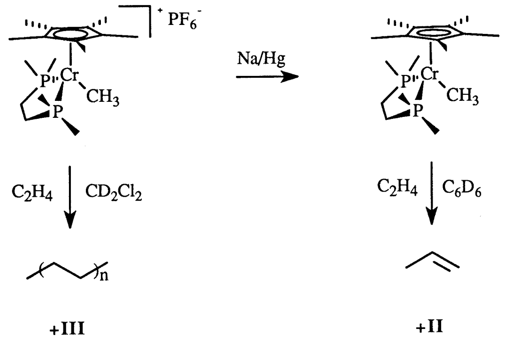
The remaining issue generating some difference of opinion is the valence state of the active chromium species. While even more contentious with regard to the Phillips catalysts, various formal oxidations states have been proposed for the Cp_2Cr/SiO_2 catalyst as well. In the words of its inventors, "it seems reasonable that the active site is an adsorbed, divalent chromium species which is still bonded to one cyclopentadienyl ligand".[7b] Our work points toward Cr^{III} rather than Cr^{II} as the active species, and even higher valence states have been contemplated.

Before describing our relevant observations some remarks of a general nature are perhaps in order. To begin with, we will consider an "active site" only a species which is actually producing polymer chains by repeated insertion of monomer. In general, this will require the presence of an alkyl (or hydride) ligand σ-bonded to chromium. Species that can be transformed into active sites by some reaction, including initiation of a chain via a reaction with ethylene, are merely "catalyst precursors". For example, the Cr^{VI} oxo sites of the calcined Phillips catalysts, or even the Cr^{II} centers resulting from reduction of the former with CO, are precursors rather than active sites. While they have the potential to catalyze the polymerization reaction, and will do so when exposed to ethylene, they are clearly missing an important attribute of the functioning catalyst, namely the growing macromolecule. While this distinction may seem rather restrictive, an unambiguous discussion of the evidence requires it. The initiation event may well change the oxidation state of the chromium (see Schemes 1 and 2), and the chemical situation is complex enough without introducing ambiguity due to ill-defined terminology.

Secondly, any argument about active vs. inactive valence states may be somewhat artificial, inasmuch as the "formal oxidation state" of a metal is a theoretical construct rather than a physical observable. Chromium complexes of the same oxidation state may have widely differing electron densities and partial charges on the metal center; the latter will ultimately determine the reactivity of any compound rather than a number based on willful neglect of any covalent contribution to metal−ligand bonding. As McDaniel put it regarding the Phillips catalysts, " it is ridiculous to speak of a particular valence state as if it were monolithic", and "the environment of the chromium, i.e., its type and arrangement of ligands, may be more important than the formal valence".[5] That said, it is probably overzealous to completely disregard valence as an important factor. There are, after all, good reasons while the concept remains in wide use in inorganic and organometallic chemistry. Furthermore, the coordination environment of the Cp_2Cr/SiO_2 catalyst is delineated fairly well. Thus, it may well be informative to ask which valence state of the metal will render a coordinatively unsaturated CpCr alkyl fragment catalytically active. In any case, in the following we will summarize our experimental observations on this matter.

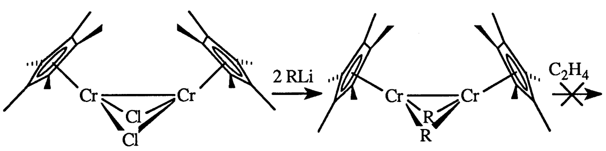
Our first experiment with respect to oxidation state was a direct comparison of the reaction of isostructural di- and trivalent chromium alkyls with ethylene. Thus, chemical reduction of $[Cp^*Cr(dmpe)Me]PF_6$ [dmpe = bis(dimethylphosphino)ethane] yielded the neutral Cr^{II} alkyl Cp*Cr(dmpe)Me, which has been structurally characterized.[12] Scheme 10 shows the side-by-side comparison of the reactivity of these two compounds.

Scheme 10



As expected, the Cr^{III} complex catalyzed the polymerization of ethylene; the forcing conditions were presumably due to the presence of the chelating phosphine, which makes the opening up of a coordination site difficult. In contrast, the Cr^{II} alkyl reacted at ambient temperature, reflecting the known substitutional lability of divalent chromium. However, its reaction with ethylene produced propene along with small amounts of other olefins. The likely mechanism of formation of propene consists of insertion of ethylene into the chromium−methyl bond, followed by β-hydrogen elimination of the resulting propyl complex. There appears to be a clear dividing line between the reactivities of these two valence states, at least in this particular system. While the Cr^{III} alkyl repeatedly favors olefin insertion (i.e. chain growth) over β-hydrogen elimination (i.e. chain transfer), the Cr^{II} species exhibits the opposite selectivity. The choice of active oxidation state for polymerization catalysis is obvious.

The set of compounds described above differ from the actual catalyst in that they contain a phosphine ligand. To assess the polymerization activity of a divalent CpCr alkyl, it would be desirable to prepare the simplest such system imaginable, i.e. "CpCrR". We have done just that, however, the resulting species were of course not mononulear compounds with 12-electron configurations. Eq. 5 depicts the synthesis of the dinuclear chromium alkyls of the type $[Cr^*Cr(\mu\text{-}R)]_2$.[41] While of interest as a novel class of organochromium compounds and precursors to chromium hydrides, these complexes did not react with ethylene. This failure is probably due to the strong metal−metal bonding featured by these dimers. The short chromium−chromium distances {e.g. 2.26 Å in $[Cr^*Cr(\mu\text{-}CH_3)]_2$} signal the strength of this interaction, which is a well-precedented feature of Cr^{II} chemistry. Only one of the dinuclear complexes, namely a benzyl complex, catalyzed the polymerization. However, upon closer inspection, we found that isomerization to a mixed valence isomer (Cr^{I},Cr^{III}) was responsible for this activity.[42]



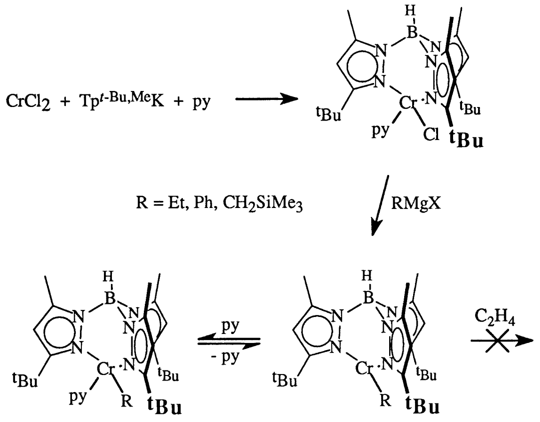
(5)

Dimerization of coordinatively unsaturated species has been noted as a "basic dilemma in attempting to model a heterogeneous reaction with compounds in solution".[14a] Thus the chemistry shown in eq. 2 is probably another good argument against the activity of dinuclear chromium sites (see above), but it falls short of ruling out mononuclear, coordinatively unsaturated Cr^{II} alkyls as active sites. However, we have recently obtained a set of compounds that address this question. Utilizing a sterically hindered tris(pyrazolyl)borate ligand, we have prepared divalent chromium alkyls of the type $Tp^{tBu,Me}CrR$ [$Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-3-methylpyrazolyl)borate; R = Et, Ph, CH_2SiMe_3], see Scheme 11.[43] The Tp ligand serves as an isoelectronic, yet sterically more demanding, replacement of the Cp ring. It effectively prevents dimerization, and accordingly the compounds feature mononuclear, four-coordinate Cr^{II}. Remarkably, they adopt an unusual "cis-divacant octahedral" coordination geometry, which leaves two coordination sites on chromium open for binding of the olefin substrate or other ligands.

None of these complexes reacted with ethylene, either at room temperature or upon heating. Indeed, $Tp^{tBu,Me}CrEt$ eventually decomposed via β-hydrogen elimination.

In summary, the available evidence suggests that divalent chromium alkyls are not capable of catalyzing the polymerization of ethylene. They either fail to react with ethylene, or, if they do, the products undergo facile β-hydrogen elim-

Scheme 11



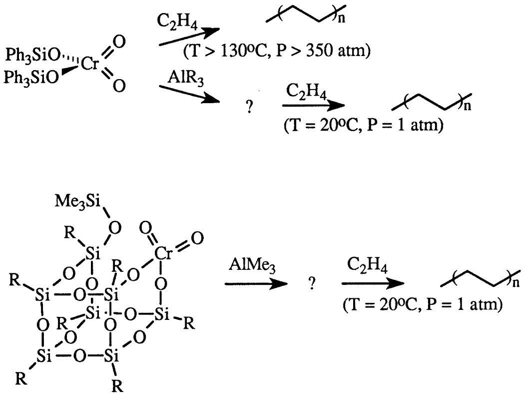
ination. Trivalent cyclopentadienyl chromium alkyls, on the other hand, when coordinatively unsaturated, consistently catalyze the polymerization, and the characteristics of the catalysis faithfully model the Union Carbide catalyst. Much less is known about the reactivity of CpCr alkyls in even higher oxidation states (IV−VI). None of the examples we[44], or others[45], have prepared have proven catalytically active, and it seems likely that the presence of several uninegative ligands beyond the Cp ligand and the polymer chain would render such complexes coordinatively saturated and hence inactive. Thus, based on the extensive available evidence from homogeneous model chemistry, we assert that the active sites of cyclopentadienyl chromium polymerization catalysts, including the Cp_2Cr/SiO_2 catalyst, are coordinatively unsaturated alkyls of trivalent chromium. To suggest otherwise would require experimental evidence in the form of a functioning homogeneous catalyst.

Other Chromium Catalysts

The most significant commercial chromium catalyst is the Phillips catalyst. It is usually prepared by impregnation of silica or silica/alumina with CrO_3, followed by calcination in air. The material resulting from this procedure is commonly thought to contain surface-bound chromate esters, i.e. Cr^{VI} species coordinated only by oxygen atoms (see Scheme 1). The oxidized form of the catalyst can be used for polymerizations. However, an induction period is observed, and products of olefin oxidation (formaldehyde) have been detected. Chromyl derivatives are known to be strong oxidants, which are reduced by olefins.[46]

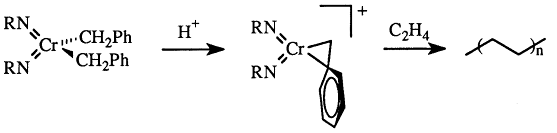
Attempts to model the activation of the Phillips catalyst in homogeneous solution have met with limited success, although without shedding much light on the detailed nature of the active site (see Scheme 12). Thus, cyclohexane solutions of bis(triphenylsilyl)chromate catalyzed the polymerization of ethylene at high temperatures ($T > 130°C$) and pressures ($P = 350-1500$ atm), even in the absence of a cocatalyst.[47] Addition of an aluminum alkyl caused "reduction of the chromium" and onset of ethylene polymerization at room temperature and atmospheric pressure. Similarly, Feher et al. have prepared and structurally characterized a chromate ester of a silasesquioxane, probably the best available structural model of the oxidized Phillips catalyst.[8b] Addition of two equivalents of $AlMe_3$ to benzene solutions of this compound produced dark orange solutions which polymerized ethylene under mild conditions (20°C, 1 atm). However, no further information about the oxidation state or chemical nature of the active catalyst(s) in these systems has been reported.

Scheme 12



It is apparent that the active site of the Phillips catalyst must contain chromium in a reduced state; however, the exact oxidation state of the metal remains unknown, despite much work and endless debate. Krauss and Stach showed some time ago that under favorable conditions the surface chromium can be reduced with carbon monoxide all the way down to Cr^{II}, and that the resulting coordinatively unsaturated species is indistinguishable in its polymerization behavior from the regular catalyst.[6] Based largely on these observations the catalytic activity of divalent chromium has become the prevailing dogma. However, the nature of the initiation step remains unclear, and the same ambiguities described for the Union Carbide catalyst (see above) exist here too. It is noteworthy that well-characterized Cr^{II} complexes, including coordinatively unsaturated alkyls, have failed to show any polymerization activity.[48]

The most promising recent development in this area has been Gibson's report of highly active homogeneous catalysts derived from bis(imido) chromium(VI) precursors (see eq. 6).[49] While the active species in this system have not yet been structurally characterized, the spectroscopic evidence seems consistent with cationic bis(imido)chromium alkyls featuring hexavalent chromium (Cr^{VI}). Based on the isolobal relationship between Cp- and imido ligands, and its putative d^0 configuration, this system resembles group IV metallocene chemistry (i.e. Cp_2MR^+) much more than any known heterogeneous chromium catalyst.



(6)

Conclusions

Coordinatively unsaturated Cp^*Cr^{III} alkyls represent the first well-characterized homogeneous ethylene polymerization catalysts based on chromium. These complexes model the Union Carbide catalyst (Cp_2Cr/SiO_2), and their chemistry may well be related to the Phillips catalyst (CrO_3/SiO_2) as well. Attachment of the compounds to inorganic oxide supports generates heterogeneous catalysts of considerable commercial potential. Looking to the future, this system may serve as the starting point for the design of new single-site catalysts containing chromium, and work toward that end is in progress in several laboratories.

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