

tions. With this approach, one may obtain additional information about known oscillatory reactions to make possible the refinement of mechanisms for those systems in which the periodic change in pH serves either as an indicator or as the governing force behind the oscillation. As studies turn increasingly toward more complex systems, particularly coupled systems, the ability to measure and control a single well-defined variable that affects multiple steps in a process will become even more crucial.

We may expect a continuing growth in the number of pH-regulated oscillators. The design approach described above is simple to apply. We note also the recent work of Nagypál and collaborators,³⁶ who use the acceleratory effect of H⁺ on a number of redox reactions to design systems capable of generating spatially propagating chemical reaction fronts.

The pH-regulated oscillators discovered thus far (and in fact, the vast majority of chemical oscillators) have been confined to redox reactions. There is no reason, however, to exclude other types of reactions from being oscillatory. For instance, preliminary calculations³⁷ show that the substitution reaction between a copper-triglycine complex and ethylenediaminetetraacetate ion, which is autocatalytic in hydroxide ion,³⁸ can serve as the starting point for a hydroxide ion oscillator in a CSTR. If we add a hypothetical OH⁻ and/or triglycine-consuming reaction to the published³⁸ mecha-

nism of this autocatalytic (nonredox) reaction, the concentration of OH⁻ undergoes oscillation.³⁷ A search for appropriate OH⁻ or triglycine-consuming steps is now under way.

Another potential application of the ideas presented here is to biological systems. Many biological processes involve coupled oscillatory reactions, and often the reactions are extremely sensitive to pH. Whether pH regulation is used as a control mechanism remains to be established. We pointed out the analogy between pH-regulated and temperature-controlled oscillations earlier. Another suggestive analogy is between the role of pH in the systems discussed here and the role of the membrane potential in neural oscillators. In the neuron, the role of an individual chemical reaction or process is played by an ion-specific conductance. The membrane potential, which is affected by all the conductances, influences the values of many of these conductances by affecting the probability of opening of the ion channels associated with a given conductance. The overall cell oscillation results from the interaction of all the channels. Thus, like the pH in a chemical system, the membrane potential affects and is affected by the activity of nearly all the "reactions" in the system. It will be interesting to see if analogies like these ultimately prove useful in transferring some of our understanding of chemical oscillators to more complex biological systems.

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Organochromium(III) Chemistry: A Neglected Oxidation State

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Chromium, the lightest and most abundant of the group 6 transition metals, has played a prominent role in the history of organometallic chemistry. While the Danish pharmacist W. C. Zeise is generally credited with the discovery of the first compound featuring a transition metal-carbon bond ("Zeise's salt", K⁺[Pt-(C₂H₄)Cl₃]⁻·H₂O, reported in 1827),¹ F. Hein's early investigation of the reaction of CrCl₃ with PhMgBr (published from 1919 on)² yielded ill-understood "Chromorganverbindungen", which remained mys-

terious until the dawn of modern organometallic chemistry in the early 1950s. Bis(benzene)chromium (1955),³ (phenylmethoxycarbene)pentacarbonylchromium, the first structurally characterized carbene complex (1965),⁴ and *trans*-iodo(phenylcarbyne)tetracarbonylchromium, the first carbyne complex (1973, all prepared in E. O. Fischer's laboratory),⁵ are other historical landmarks on the path toward understanding the metal-carbon bond.

Chromium compounds also find use as catalysts, adding a utilitarian dimension to the study of its or-

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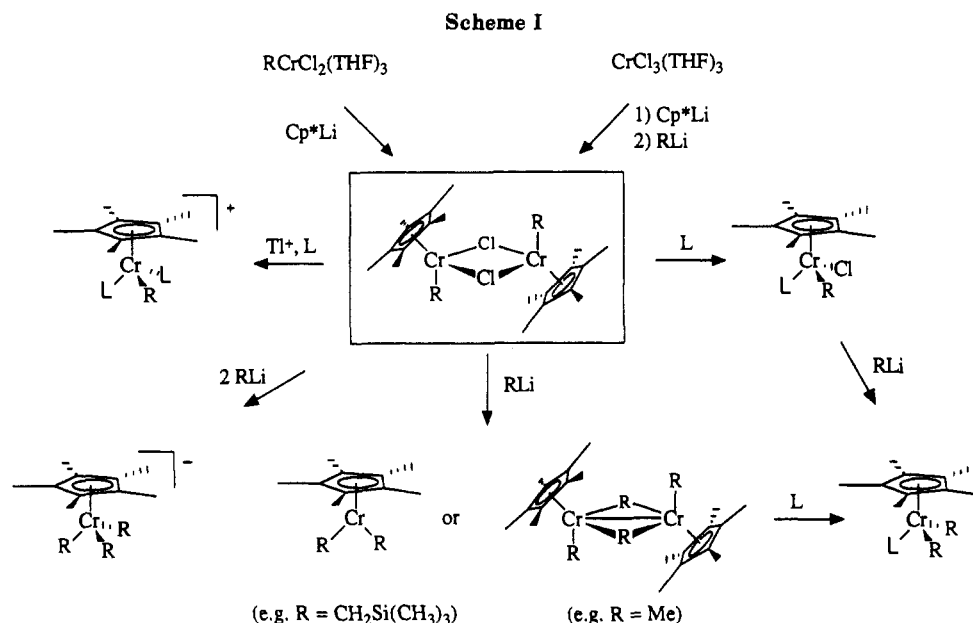
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ganometallic chemistry. Aside from minor applications in the hydrogenation of conjugated dienes⁶ and hydrocarbon oxidation,⁷ by far the most important role of chromium catalysis is in the polymerization of small olefins (ethylene, propene) using heterogeneous catalysts.⁸ However, much of the known organometallic chemistry of chromium concerns low-valent carbonyl derivatives and/or diamagnetic complexes with 18-electron configurations.⁹ Such molecules are unlikely candidates for modeling highly reactive (coordinatively unsaturated) and oxide-supported chromium alkyls. Therefore we felt that an investigation of chromium alkyls in higher oxidation states and with unpaired electrons might uncover novel compounds and unusual reactions and have some relevance to commercially used catalysts. The following is a summary of our work on a new class of paramagnetic chromium(III) alkyls. Organometallic derivatives of chromium in this oxidation state have been reported previously,¹⁰ but their limited stability and paramagnetic nature have prevented the development of their chemistry. Of special note in this context are the unusual aquo alkyls of the type [RCr(H₂O)₅]²⁺,¹¹ which serve as a bridge between organometallic chemistry and the realm of inorganic coordination compounds.

Synthesis

Cyclopentadienyl ligands tend to kinetically stabilize transition-metal alkyls, and thus we began by exploring the synthesis of mixed cyclopentadienyl(alkyl)chromi-

um(III) complexes (cyclopentadienyl represents both $\eta^5\text{-C}_5\text{H}_5$ (Cp) and $\eta^5\text{-C}_5\text{Me}_5$ (Cp*)). Initially solvated chromium(III) alkyls of the type $\text{RCrCl}_2(\text{THF})_3$ served as starting materials,¹² but eventually we found that treatment of $\text{CrCl}_3(\text{THF})_3$ with 1 equiv of, e.g., Cp^*Li , followed by addition of the lithium alkyl reagent of choice to the $[\text{Cp}^*\text{CrCl}_2]_2$ generated in situ, yielded dimeric alkyl complexes of the formula $[\text{Cp}^*\text{Cr}(\text{R})\text{Cl}]_2$ in a convenient procedure and high yield. This synthesis proved general (i.e., R = methyl, ethyl, *n*-butyl, phenyl, benzyl, neopentyl, and (trimethylsilyl)methyl), and the complexes are purple crystalline solids, which dissolve readily in common organic solvents. They are sensitive to air and moisture, but thermally reasonably stable. Scheme I shows various further transformations leading to several series of neutral, anionic, or cationic half-sandwich complexes with one to three alkyl groups coordinated to chromium.¹³ Thus there are now available for reactivity studies a wide variety of stable chromium(III) alkyls. These compounds obviously do not adhere to the familiar 18-electron rule¹⁴ and exhibit odd numbers of valence electrons. Their most common electron count is 15, but some unsaturated derivatives with 13-electron configurations have also been prepared.

Structure

The paramagnetic nature of the compounds under consideration renders NMR spectroscopy much less useful for assigning structures.¹⁵ Consequently structural characterization by X-ray diffraction has played an important role in the development of this chemistry.

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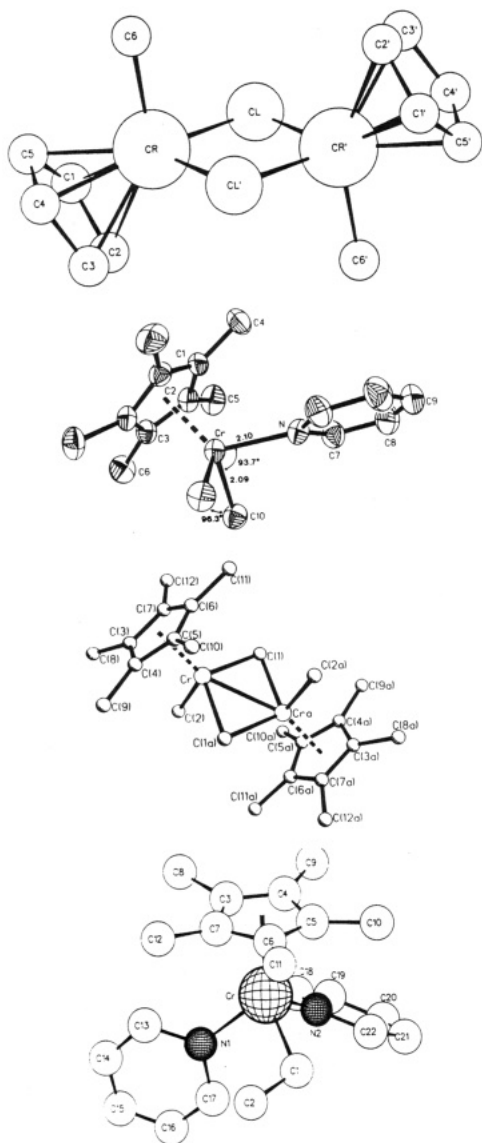


Figure 1. Molecular structures of representative chromium(III) alkyls. From top to bottom: $[\text{CpCr}(\text{CH}_3)\text{Cl}]_2$,^{13a} $\text{Cp}^*\text{Cr}(\text{py})(\text{CH}_3)_2$,^{13b} $\text{Cp}^*\text{Cr}(\text{Py})_2\text{CH}_2\text{CH}_3]^+\text{PF}_6^-$ (only cation is shown),^{13c} and $[\text{Cp}^*(\text{CH}_3)\text{Cr}(\mu\text{-CH}_3)]_2$.^{13e}

Figure 1 depicts selected results of single-crystal structure determinations representative of some of the structures in Scheme I. The recurring motif (of over a dozen structures) is the pseudooctahedral coordination of chromium comprising one cyclopentadienyl ligand, which occupies three adjacent coordination sites, and three monodentate ligands (alkyl, halide, neutral Lewis base, etc.). The angles between the monodentate ligands only slightly exceed the ideal 90° (typical averaged values are $92\text{--}97^\circ$). This structural preference presumably reflects the large ligand-field stabilization of a d^3 ion in an octahedral coordination environment.¹⁶ The cyclopentadienyl ring is always bound in an η^5 fashion with the average $\text{Cr}\text{-C}_{\text{ring}}$ distance in the range $2.19\text{--}2.30 \text{ \AA}$. The carbon-carbon distances within the aromatic rings are similar and average between 1.39 and 1.43 \AA (depending on the compound). The methyl groups of the pentamethylcyclopentadienyl ligands are consistently bent out of the plane of the C_5 ring and

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away from the metal (averages range between 1° and 4°).¹⁷ The average chromium-carbon σ -bond measures $2.09 (1) \text{ \AA}$ and varies little from molecule to molecule. These distances as well as $\text{Cr}\text{-N}$ distances of several pyridine complexes and $\text{Cr}\text{-Cl}$ distances of those derivatives with terminal chloride ligands consistently point to a covalent radius of ca. 1.32 \AA for chromium(III) within this class of compounds.

Several of the structurally characterized complexes contain more than one chromium atom. These molecules can be thought of as sharing edges or faces of the basic octahedral units. Depending on the bridging ligands, they may exhibit close chromium-chromium contacts, and the question of metal-metal bonding must be addressed.¹⁸ While metal-metal distance is most frequently cited as a criterion for the presence and order of such bonds,¹⁹ there clearly exists a continuum of interactions of adjacent metal atoms and other physical properties, and theoretical considerations come into play (see below).

Spectroscopy and Magnetism

The importance of multinuclear NMR spectroscopy for the rapid development of transition-metal organometallic chemistry during the past 35 years is hard to overestimate.²⁰ While the technique is uniquely suited for the study of diamagnetic substances (a possible reason for the organometallic chemists' historical preoccupation with closed-shell species), its application to paramagnetic compounds is less straightforward and informative.¹⁵ The resonances are isotropically shifted and broadened severely (due to long electron-spin relaxation times) so as to obscure any coupling. Protons in the α -position to the metal are generally unobservable as are nuclei other than ^1H (e.g., ^{13}C , ^{31}P), and the large peak width makes integrations less reliable. Thus NMR spectroscopy is only modestly helpful in the initial characterization of chromium(III) complexes; however, once a compound has been identified, the spectroscopic data can be used to confirm its production in another reaction or to monitor its chemical transformations. It has been shown that ^2H NMR spectra of deuteriated chromium(III) complexes feature much narrower resonances,²¹ but the expense and effort involved in preparing labeled derivatives will be justifiable only in special cases.

Indispensable for the characterization of complexes with unpaired electrons are measurements of the magnetic susceptibility.²² The determination of the effective magnetic moment and its temperature dependence allows assignments of oxidation state, spin state, and possible metal-metal interactions to be made. Figure 2 shows some typical results of measurements on solid samples performed with a Faraday balance. The mononuclear complex (Figure 2, top) exhibits simple Curie-Weiss behavior ($1/T$ dependence of χ_m), and the effective magnetic moment of $\mu_{\text{eff}} = 4.14 \mu_B$ is con-

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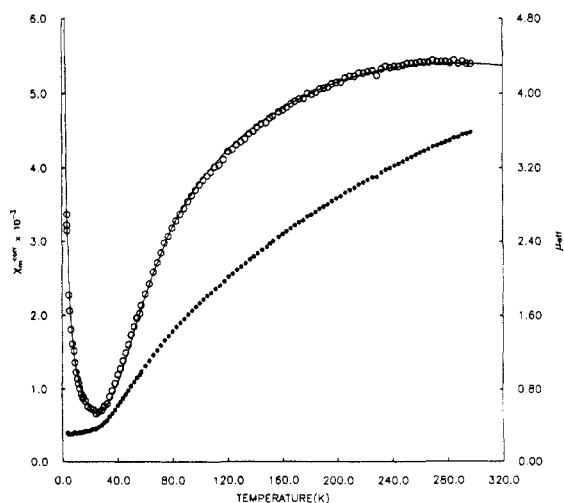
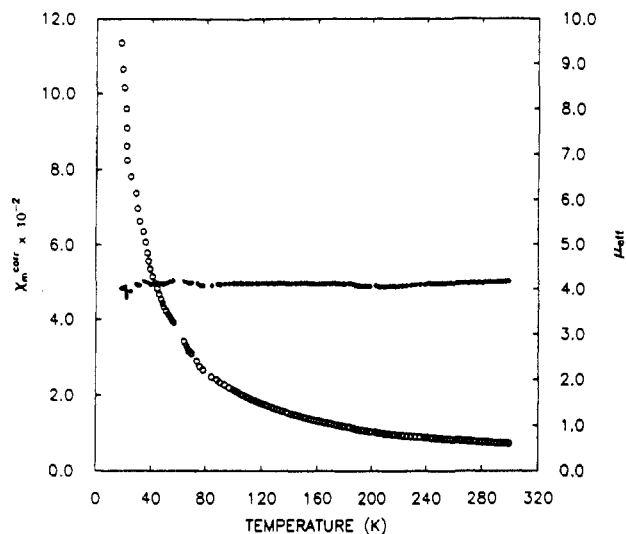


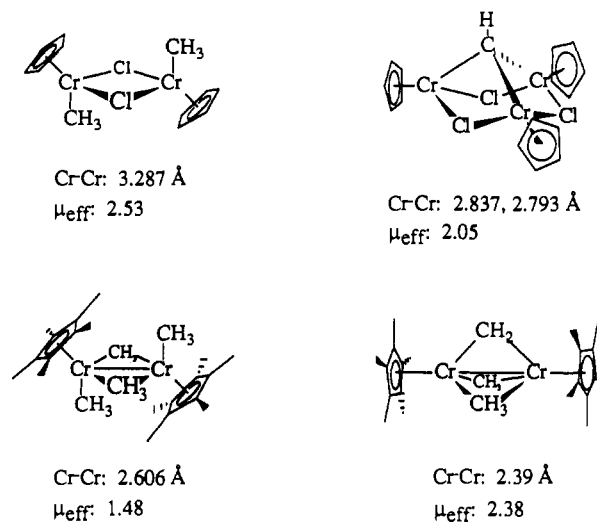
Figure 2. Temperature dependence of molar magnetic susceptibility (χ_m , open circles) and effective magnetic moment (μ_{eff} , filled circles) of $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{CH}_3]^+\text{PF}_6^-$ (top) and $[\text{CpCr}(\text{CH}_3)\text{Cl}]_2$ (bottom).

sistent with the presence of three unpaired electrons.²³ Figure 2 (bottom) depicts the results obtained for the dimeric complex $[\text{CpCr}(\text{Me})\text{Cl}]_2$, which contains two chromium atoms situated at a distance of ~ 3.3 Å. μ_{eff} is temperature dependent and at no time approaches a value consistent with three unpaired electrons per chromium ($5.5 \mu_B$ for the dimer). This magnetic behavior is characteristic of *antiferromagnetic coupling* of the two $S = 3/2$ centers.²⁴ Interaction of the unpaired spins, presumably through the bridging ligands, results in a manifold of spin states ($S = 0, 1, 2, 3$). The singlet state is lowest in energy, but is separated from the excited states only by small energies, allowing for thermal population of states with higher multiplicity with increasing temperature and thus giving rise to an increase in μ_{eff} . Fitting of the susceptibility data with a theoretical expression allows the determination of the coupling constant J ($2J$, $6J$, and $12J$ being the energy

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Scheme II



differences between the $S = 0$ and $S = 1, 2$, and 3 states, respectively). Typical values of J for these compounds are around -50 cm^{-1} .¹³

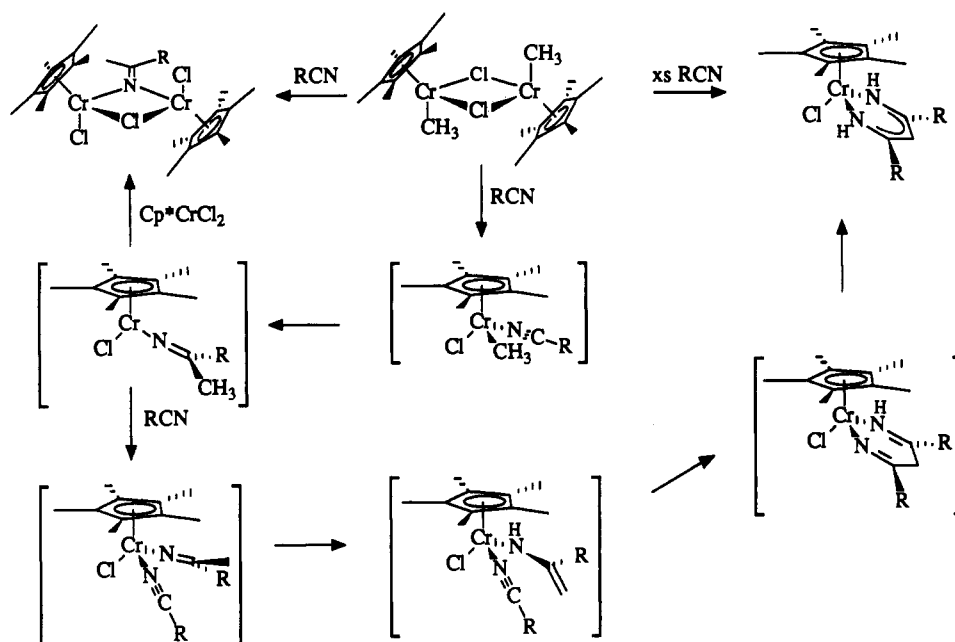
However, as the Cr(III) centers get closer to each other, the potential for a direct interaction increases and eventually leads to significant metal-metal bonding. Pairing of spins in bonding molecular orbitals should lower the number of unpaired electrons and thus the magnetic moment. Scheme II shows a series of complexes with decreasing Cr(III)-Cr(III) distances and their associated effective magnetic moments (per chromium atom!). $[\text{Cp}^*\text{Cr}(\mu\text{-CH}_2)]_2(\mu\text{-CH}_2)$, the molecule with the shortest Cr(III)-Cr(III) distance known,^{13f} appears to deviate from the trend; note, however, that it features two octahedra sharing a face rather than an edge, and thus the d-orbital interactions are different. On the basis of a detailed theoretical analysis,²⁵ we believe that significant metal-metal bonding occurs in those complexes with very short Cr-Cr distances (indicated in Scheme II). The key to forcing the metal atoms together appears to be bridging ligands which engage in three-center, two-electron bonding (e.g., bridging methyl groups).^{13e} This core level effect in a synergistic fashion increases the splitting of the frontier d orbitals, leading to pairing of electrons in MOs which are metal-metal bonding in character. Many polynuclear Cr(III) complexes with bridging ligands have been investigated structurally and magnetically over the years, and all were thought to exhibit repulsive interactions between the metal centers.²³ The use of non-traditional alkyl ligands has thus enabled us to contribute to the unfolding story of metal-metal bonding, a domain of traditional inorganic chemistry.

Reactivity

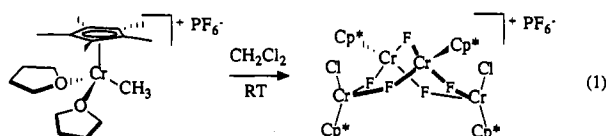
Possibly the most widely appreciated limitation to the preparation of isolable transition-metal alkyls is their tendency to decompose by β -hydrogen elimination (i.e., the transfer of hydrogen from the β -position of a σ -bonded alkyl to the metal accompanied by release of olefin). However, this reaction does not appear to be facile for chromium(III) alkyls, judging by the isolation of various derivatives containing β -hydrogens. An appreciable barrier to β -elimination is of course crucial for

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Scheme III



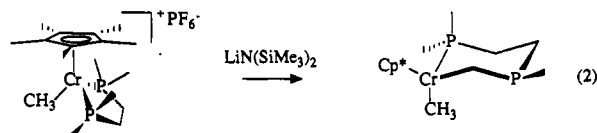
metals involved in polymerization catalysis, as it limits chain growth (see below). We believe that the stability of these molecules is limited by the inherent metal-carbon bond strength (i.e., decomposition by homolysis) or by intermolecular activation of C-H bonds of the alkyl ligands. To wit, [CpCr(CH₃)(μ-Cl)]₂ upon gentle heating decomposes to [CpCr(μ-Cl)]₃(μ₃-CH),^{13a} the methylidyne ligand of which is thought to originate in a methyl group, and the dimer [Cp*Cr(CH₃)(μ-CH₃)]₂ slowly decomposes at room temperature into [Cp*Cr(μ-CH₃)]₂(μ-CH₂) and methane.^{13f} Coordinatively unsaturated, highly Lewis acidic intermediates are likely responsible for such reaction pathways, and the same character is also evident in the ready abstraction of halide from various sources (e.g., eq 1).²⁶



The formal oxidation state of the metal greatly influences the chemistry of organometallics, and redox reactions represent an underutilized dimension of control over their reactivity. We are using electrochemical techniques (cyclic voltammetry, coulometry) to investigate the stability of chromium alkyls in oxidation states other than III. For example, the cyclic voltammogram of the cationic [Cp*Cr(dmpe)CH₃]⁺PF₆⁻ (dmpe = bis(dimethylphosphino)ethane) in THF solution exhibited a reversible reduction at -1.9 V vs the ferrocene/ferrocene reference couple. Subsequently, chemical reduction with sodium amalgam yielded the chromium(II) alkyl Cp*Cr(dmpe)CH₃, which was characterized structurally by X-ray diffraction.²⁷ While this complex features an even 16-electron configuration, it is still paramagnetic and exhibits a temperature-independent effective magnetic moment consistent with two unpaired electrons. Oxidation on the other hand

not yielded tractable alkyl complexes of Cr(IV) or higher oxidation states in our hands. The cyclic voltammogram of NEt₄⁺[Cp*Cr(CH₃)₃]⁻ showed an oxidation wave at -1.4 V vs Fc⁺/Fc, but this was irreversible even on the electrochemical time scale.²⁸ Chemical oxidation of this species with Ag⁺BF₄⁻ in the presence of pyridine as a trapping agent yielded the chromium(III) complex Cp*Cr(py)(CH₃)₂. It seems likely that oxidation initially yields Cp*Cr^{IV}(CH₃)₃, but this complex decomposes by loss of a methyl radical, leaving Cp*Cr^{III}(CH₃)₂ to be trapped by pyridine. The apparent instability of the chromium(IV) alkyl is somewhat surprising, as the isoelectronic vanadium complexes of the type CpV(L)R₂ (d²) are perfectly stable²⁹ and there exist also chromium(IV) compounds of the type CrR₄.³⁰

Another elementary facet of reactivity is acid/base chemistry. The metal-carbon bond is of course polar, and the chromium alkyl complexes react with acids as weak as *tert*-butyl alcohol or trialkylammonium salts, producing alkane. Conversely, we wondered whether deprotonation of a chromium-bound alkyl might be possible. A positive charge on the complex should increase its acidity, and thus [Cp*Cr(dmpe)CH₃]⁺PF₆⁻ was treated with LiN(TMS)₂. Deprotonation did indeed occur, but not in the hoped for sense (see eq 2).³¹



Insertion of Polar Organic Molecules

Very early in the exploration of the reactivity of the chromium(III) alkyls, and quite fortuitously, we dis-

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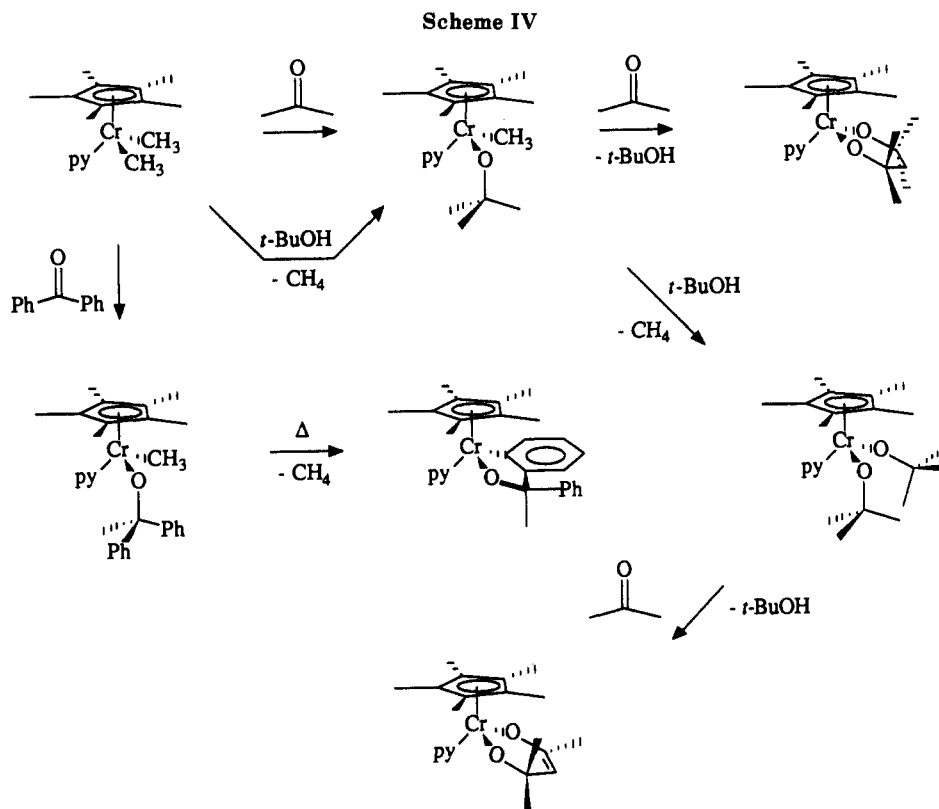
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covered that the alkyl dimers $[\text{Cp}^*\text{Cr}(\text{R})\text{Cl}]_2$ reacted with nitriles.^{13b,d} Exposure of these complexes to an excess of nitrile readily yielded nitrogen-containing heterocycles, which could be thought of as being derived from β -diketonates by substitution of the oxygen atoms with NH groups (see Scheme III). These β -diketimino complexes resulted inter alia from an insertion of the unsaturated organic molecule into the chromium-carbon bond. While transition-metal alkyls are well-known to undergo so-called "migratory insertion" reactions with a variety of unsaturated functional groups (e.g., CO, alkynes, alkenes, isonitriles), there are only a few reports of insertions of nitriles.³² The compounds exhibiting this reactivity typically contain highly Lewis acidic early transition metals, lanthanides, or actinides. To the best of our knowledge our chromium system features the "latest" (i.e., rightmost in the periodic system) metal to undergo this reaction, and we believe that its relatively high oxidation state and the electronic unsaturation of the compounds are responsible for this unusual behavior.

Evidence for the presumed ketimino intermediates resulting from the first insertion step was obtained by running the reaction at low nitrile concentration. Under these circumstances the reaction products were not the β -diketimino complexes but rather dinuclear compounds containing a bridging ketimino ligand. The complex obtained from the reaction of $[\text{Cp}^*\text{Cr}(\text{CH}_3)_2\text{Cl}]_2$

with benzonitrile has been structurally characterized. Treatment of these complexes with more nitrile did not result in any further reaction. Thus they represent the result of irreversible trapping of the coordinatively unsaturated true intermediate, which in the presence of an excess of nitrile produces the diketimino moiety. A reasonable series of transformations following this branching point consists of an imine/enamine tautomerization followed by nucleophilic attack of the enamine on a second coordinated nitrile, and finally another hydrogen shift completes the overall reaction (see bracketed structures in Scheme III).

The application of organometallic transformations, both stoichiometric and catalytic, in organic synthesis is becoming increasingly popular. The main role of chromium in this regard has been in the elaboration of carbene complexes (i.e., the Dötz reaction).³³ We have found that chromium(III) alkyls readily react with ketones,³⁴ one of the most common functional groups in organic chemistry. Scheme IV depicts the results of reactions of a readily available chromium dialkyl with the representative substrates acetone and benzophenone. Insertion into the first chromium-carbon bond is rapid and yields chromium alkoxides. In the case of benzophenone, the newly formed alkoxide ligand on gentle heating suffers an ortho-metalation. This selective functionalization of a phenyl ring may prove synthetically useful. The *tert*-butoxide ligand resulting from the insertion of acetone does not undergo an analogous metalation. Rather it functions as a base in the reaction with further acetone. Proton transfer is favored over a second insertion, which would yield the independently prepared bis(*tert*-butoxide) complex. A

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likely mechanism for the formation of the chelating bis(alkoxide) involves an alkyl(enolate) complex, which may rearrange to an oxametallacyclobutane, followed by an insertion of a third molecule of acetone into the chromium-carbon bond of the metallacycle. The deuterium labeling pattern of the product of a reaction of $\text{Cp}^*\text{Cr}(\text{py})(\text{CH}_3)(\text{O}^t\text{Bu})$ with acetone- d_6 was consistent with this hypothesis, i.e., the protons originating in a chromium-bound methyl group ended up exclusively in one of the methyl groups of the 2,4-dimethyl-2,4-pentanediol liberated upon protonation of the chromium complex. In any case, the overall reaction represents the coupling of two ketones via an intervening methylene group, an unusual transformation.

A different coupling reaction ensues upon treatment of the chromium alkoxide complex $\text{Cp}^*\text{Cr}(\text{py})(\text{O}^t\text{Bu})_2$ with acetone. Liberation of 2 equiv of *tert*-butyl alcohol and coupling of the enolate ligands yield a doubly deprotonated β -hydroxy ketone ligand. Unfortunately this moiety is not basic enough to deprotonate additional acetone, thus precluding a chromium-catalyzed aldol condensation.³⁵

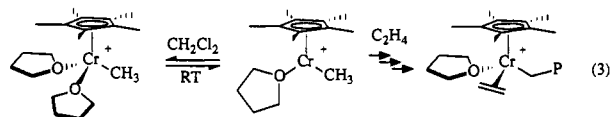
Despite the apparent similarity of the above reactions to alkylations of ketones with carbanions (e.g., RLi , RMgX), the available precedent for the insertion of ketones into transition-metal alkyls is limited to titanium and zirconium complexes.³⁶ Coordination of the resulting alkoxide ligand to a transition metal may open pathways for further elaboration. In addition, utilization of optically active coligands on the substitutionally inert Cr^{III} center holds the potential for enantioselective transformations.

Ethylene Polymerization

Polyethylene production worldwide relies heavily on chromium-based catalysts.³⁷ Broadly speaking, two types of catalysts are used commercially. The so-called Phillips catalyst is prepared by deposition of CrO_3 on silica followed by activation with hydrogen.³⁸ On the other hand, Union Carbide has developed catalysts formed by treatment of silica with low-valent organometallic compounds, most notably chromocene (Cp_2Cr).³⁹ Questions about the chemical nature of the active site(s), the oxidation state of the active chromium, and the mechanism of initiation have been the subject of a longstanding debate, which continues to this day.⁴⁰ Motivated by an apparent similarity be-

tween our compounds and the proposed active site of the $\text{Cp}_2\text{Cr}/\text{SiO}_2$ catalyst, we began an investigation of the reactions of our chromium(III) alkyls with small olefins.

Availability of a coordination site for the olefin proved crucial. The first active catalyst we discovered was the cationic complex $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{CH}_3]^+\text{BPh}_4^-$.^{13c} While the THF ligands in this complex were bound strongly enough to allow its isolation and even the determination of its crystal structure, in CH_2Cl_2 solution a dissociation equilibrium was established. We have no information about the exact resting state of the active catalyst (coordination of CH_2Cl_2 or ethylene?), but the coordinatively unsaturated 13-electron species $[\text{Cp}^*\text{Cr}(\text{THF})\text{CH}_3]^+$ is a reasonable candidate (eq 3).



Rapid repetitive coordination and migratory insertion of ethylene yielded high-density polyethylene at ambient temperature and 1-atm pressure. Characterization of various polymer samples by gel permeation chromatography showed relatively low molecular weights (M_n 10 000–20 000, M_w 23 000–77 000) and narrow molecular weight distributions (M_w/M_n 1.6–4.6).⁴¹ Addition of THF to the catalyst solution dramatically slowed the polymerization, consistent with an obligatory dissociation of a ligand from the catalyst precursor.

The cationic nature of this catalyst nicely complements the emerging notion that positively charged alkyls comprise the active sites of Ziegler-Natta catalyst preparations based on group 4 elements.⁴² However, we subsequently found other neutral complexes (e.g., $\text{Cp}^*\text{Cr}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_2$) which catalyze the rapid polymerization of ethylene even at low temperatures (-40°C). It thus appears that coordinatively unsaturated chromium(III) alkyls are efficient ethylene polymerization catalysts, independent of their charge. The oxidation state of the chromium seems to make a difference, however. While controversial, the active site of the $\text{Cp}_2\text{Cr}/\text{SiO}_2$ catalyst has been proposed to contain divalent chromium (Cr^{II}).³⁹ We have addressed this question with a direct comparison of the reactions of a pair of isostructural Cr^{III} and Cr^{II} complexes with ethylene. $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{CH}_3]^+\text{PF}_6^-$ was very slow to react with C_2H_4 , presumably due to the great reluctance of the chelating phosphine to open the required coordination site. However, upon heating to 90°C , polyethylene was produced. In contrast, neutral $\text{Cp}^*\text{Cr}(\text{dmpe})\text{CH}_3$ reacted with ethylene at ambient temperature, but the major product of this reaction was propene. The latter must be formed by insertion of ethylene into the chromium(II)-methyl bond followed by a β -hydrogen elimination. The relative rates of olefin

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insertion (chain growth) versus β -elimination (chain transfer) are apparently very different in the two oxidation states, favoring the former with Cr^{III} compounds and the latter for Cr^{II} alkyls. An obvious explanation for this difference lies in the superior stabilization of coordinated olefin by the more electron rich d⁴ ion due to back-bonding. Our results clearly suggest that trivalent chromium is responsible for the polymerization activity of chromium-based catalysts. Further experiments in this area will be designed to elucidate the factors that govern the critical properties of the polymer (i.e., molecular weight, dispersity, branching, etc.).

A Look Ahead

We have shown that a wide variety of chromium(III) alkyls can be prepared and that such molecules are highly reactive. The chromium-carbon bonds in these compounds appear to be fairly polar, and the complexes are very Lewis acidic. As a result of this character, insertion reactions with unsaturated organic molecules as well as intramolecular C-H activation processes are very facile.

Where to go from here? Somewhat surprisingly, hydrogen does not react with many of the alkyl complexes, even under forcing conditions. Thus the preparation of chromium(III) hydrides and the study of their reactivity remain a challenge for the future. Similarly the exploration of the organometallic chem-

istry of chromium in oxidation states even higher than III remains to be tackled. Finally, an area in which we have some promising preliminary results concerns the question of chromium-carbon multiple bonds (i.e., alkylidenes and alkylidynes). Several of the compounds mentioned throughout this Account catalyze the ring opening metathesis polymerization (ROMP) of norbornene,⁴³ hinting of the accessibility of a chromium alkylidene complex. The isolation and characterization of such molecules is anticipated.

Paramagnetic organometallic compounds and their chemistry remain a challenging field of study. For the element chromium, such molecules may well be more relevant to catalytic reactions than their diamagnetic 18-electron counterparts. We are continuing our exploration. Stay tuned!

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Additions and Corrections

Vol. 22, 1989

Robert D. Guthrie* and William P. Jencks: IUPAC Recommendations for the Representation of Reaction Mechanisms.

Page 346, column 2. The word electrofugic on the line above eq 2 should be replaced by the word nucleofugic.