

# Paramagnetic organometallic compounds – The example chromium

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The historical development of organometallic chemistry is marked by a heavy emphasis on the synthesis and characterization of closed shell molecules that obey the 18-electron rule. In contrast, the goal of our research is the exploration of the reaction chemistry of paramagnetic organometallics. For example, our investigation of chromium alkyls in various oxidation states (notably + III) featuring unpaired electrons has uncovered a wide variety of novel compounds and unusual reactions. Our results are also relevant to the commercial use of chromium catalysts for the polymerization of ethylene. While the study of paramagnetic organotransition metal compounds is associated with certain difficulties, the potential rewards amply merit the special effort.

## Introduction

THE origin of organometallic chemistry, i.e. the realm of molecules with direct metal–carbon bonds, is usually traced back to the preparation of Zeise's salt, i.e. the ethylene complex  $K^+[Pt(C_2H_4)Cl_3]^-$ , in 1827 by W. C. Zeise<sup>1</sup>, even though this Danish pharmacist did not fully appreciate the nature of the compound he had obtained. Other landmark discoveries during the early development were the preparation of  $Ni(CO)_4$ , the first homoleptic metal carbonyl, prepared by Mond in 1890 (ref. 2), and the discovery of cobalt catalysed hydroformylation by Roelen in 1938 (ref. 3). Grignard reagents as well as other main group alkyls (e.g. Li, Al, Zn) have proven to be of immense value in the development of organic chemistry. However, the 'modern area' of organometallic chemistry began as recently as 1951, when Pauson and Miller independently – and serendipitously – discovered ferrocene,  $(\eta^5-C_5H_5)_2Fe$  (ref. 4). The novel 'sandwich structure' and the unusual stability of this transition metal alkyl attracted the interest of many researchers. The latter half of the 20th century has seen an almost explosive growth of organometallic chemistry, which is now one of the most active subdisciplines of chemistry. This interest is fueled by the discovery of whole new classes of compounds and by the new impulses the field has given to catalysis, materials science and organic synthesis.

## The rule of 18-electron configurations and diamagnetism

One of the guiding principles of organometallic chemistry to emerge very early on was the 18-electron rule<sup>5</sup>. In essence, this rule predicts that organometallic compounds of transition metals will be stable when the valence shell of the metal contains 18 electrons.  $Cr(CO)_6$  is a good example of a complex that obeys this rule, as the six valence electrons of a neutral chromium atom combine with the twelve electrons donated by the lone pairs (2 electrons each) of the six CO-ligands. There are many ways to rationalize this rule, and a simple one is the analogy to the familiar octet rule prevailing in carbon chemistry. Thus, a transition metal has nine valence atomic orbitals (five nd, one  $(n+1)s$ , and three  $(n+1)p$ ), and a completely filled valence shell with eighteen electrons (i.e. the electron configuration of a noble gas) presages stability. The loss of a ligand (e.g. a CO molecule from  $Cr(CO)_6$ ) then leaves the metal with only 16 electrons, i.e. 'coordinatively unsaturated'. Many reaction mechanisms have been written based on this interplay between stable 18-electron compounds and reactive 16-electron species. Indeed, one of the original formulations of the 18-electron rule read thus: 'Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons'<sup>5</sup>.

A corollary of this heavy emphasis on closed shell species and even numbers of electrons has been the domination of organometallic chemistry by diamagnetic compounds. In many ways organometallic compounds behave like organic ones (a notable exception being their beautiful colours!), and one of the most striking parallels is the utility of routine NMR spectroscopy for their characterization. The advent of even more powerful, multinuclear NMR techniques has played a crucial role in the rapid development of our understanding of the structures and reactions of organometallic compounds<sup>6</sup>. It has come to the point where some chemists, faced with a compound that does not exhibit a 'normal'  $^1H$  NMR spectrum, discard it and move on to a more promising project. In effect, our addiction to NMR spectroscopy has allowed the 18-electron rule to become a set of blinders limiting our view of the field. We need to take a step back and reconsider.

Although the 18-electron rule provides a useful guideline concerning the stability of organometallic complexes,

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there exist many exceptions to it. In chromium chemistry, for example, we need to look no further than to chromocene,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}$ , a 16-electron complex with two unpaired electrons (i.e. a triplet ground state). This paramagnetic compound ( $\mu_{\text{eff}} = 3.2 \mu_{\text{B}}$ ) exhibits a very broad  $^1\text{H}$  NMR resonance at ca 324 ppm, and its  $^{13}\text{C}$  NMR resonance has been located at  $-325 \text{ ppm}$ <sup>7</sup>. Despite these inconvenient and somewhat uninformative NMR data, chromocene is a very interesting molecule; for example, when supported on silica it forms a highly active ethylene polymerization catalyst (see below). Indeed, examples of organometallic compounds with unpaired electrons abound. This is not too surprising when one considers that organometallic molecules are just special types of coordination compounds, many of which are paramagnetic. It is also important to realize that the 18-electron rule holds most strongly for metals in low formal oxidation states and coordinated by small strong-field ligands (e.g. H, CO, alkyls, etc.). Interestingly, even in this area the appreciation for odd-electron species (17- and 19-electron molecules) and their reactivity has been steadily growing<sup>8</sup>. For example, associative substitution reactions of 17-electron metallaradicals (e.g.  $\text{V}(\text{CO})_6$ ) are orders of magnitude faster than the comparable reactions of 18-electron species<sup>9</sup>.

In any event, it is now clear that the 18-electron rule is a useful guideline, but no more, and that diamagnetism is not a defining attribute of transition metal organometallics. There are already many paramagnetic examples known, and – more importantly – many more remain to be discovered and their reactivity investigated.

Based on these considerations, some time ago we initiated a study of organochromium complexes in the +III oxidation state<sup>10</sup>. The electronic configuration of Cr(III) ( $d^3$ ) ensures paramagnetism of such complexes. We began this work with the expectation that an exploration of chromium(III) alkyls might lead to the discovery of novel and useful chemistry. In the following paragraphs we survey our findings, which eventually came to pertain to other formal oxidation states of chromium as well.

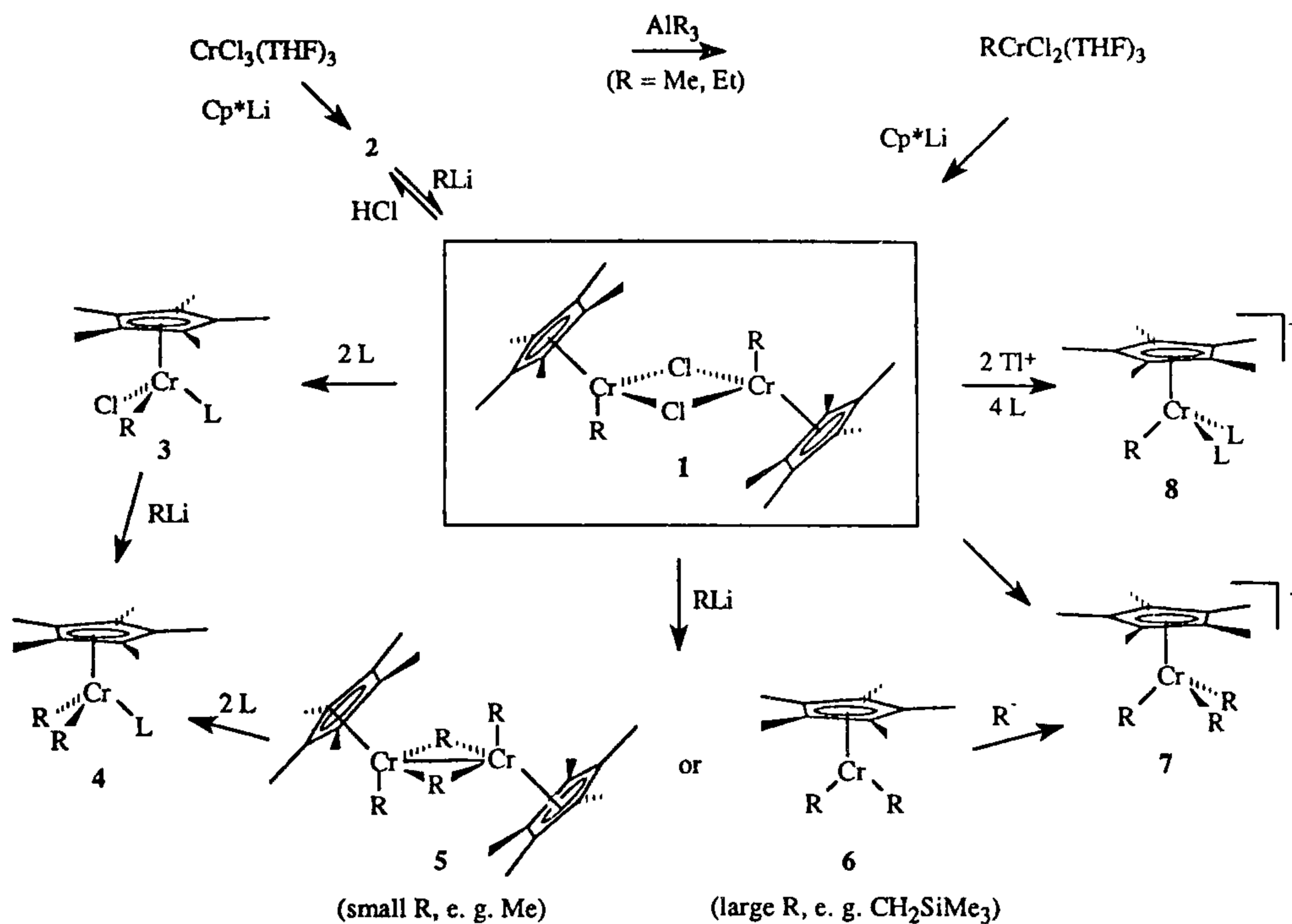
### Paramagnetic chromium alkyls

We were by no means the first to prepare Cr(III) alkyls. There existed a variety of solvated molecules of the type  $[\text{CrR}_n\text{X}_m\text{S}_c]^{n+/m-}$  (R = alkyl, aryl; X = halide; S = solvent, e.g. THF, pyridine, etc.)<sup>11,12</sup>. Of particular note was a series of aquo alkyls of the constitution  $[\text{RCr}(\text{OH}_2)_5]^{2+}$  (ref. 13), which not only violated the 18-electron rule, but also ran counter to the received wisdom that metal–carbon bonds are subject to rapid hydrolysis. However, our studies represent the first systematic investigation of the syntheses, structures, and reactivities of a broad class of paramagnetic chromium alkyls featuring cyclopentadienyl ligands.

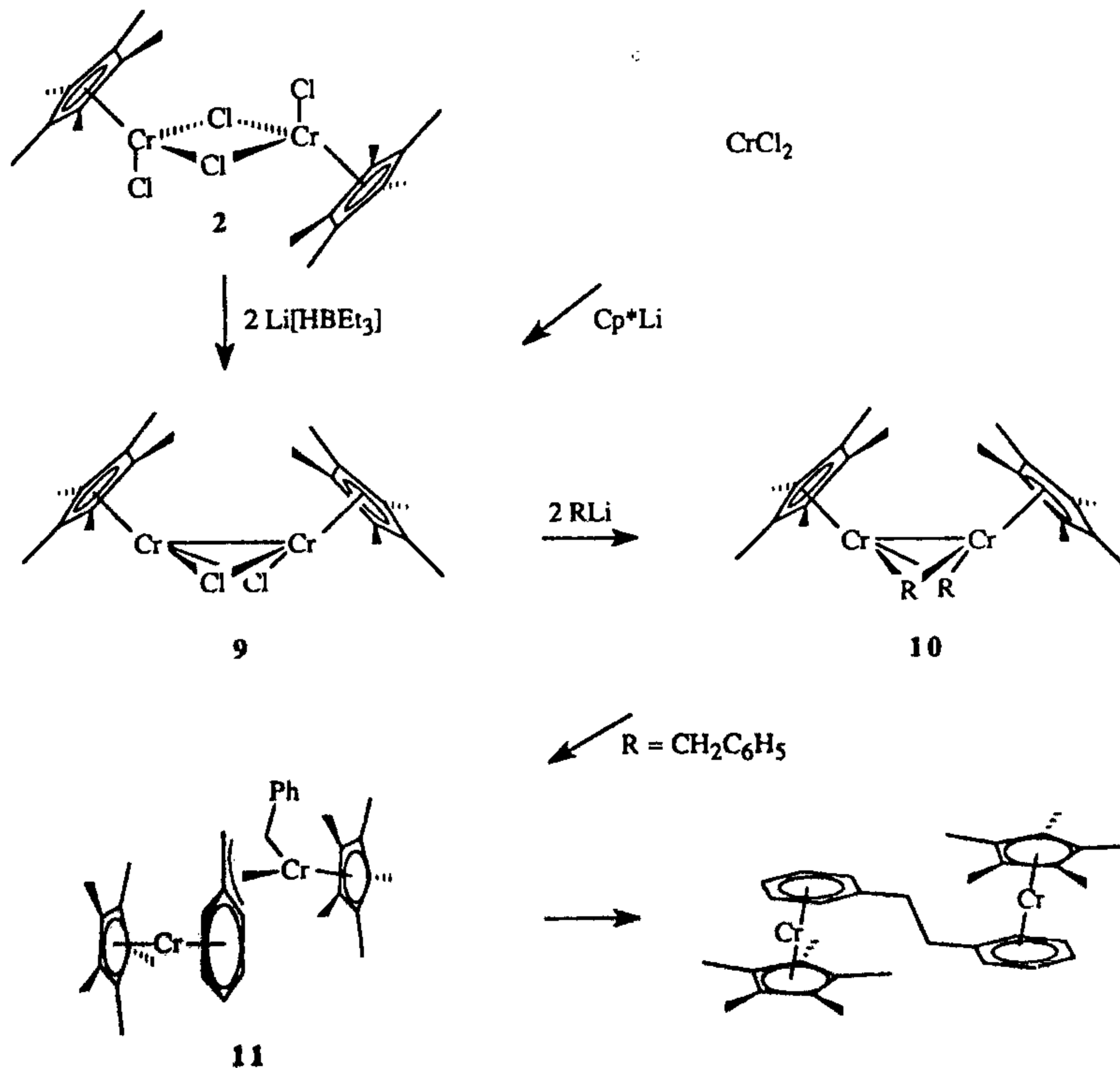
Most of our work has utilized the pentamethylcyclopentadienyl ligand ( $\eta^5\text{-C}_5\text{Me}_5$ , abbr. Cp\*), a very popular ancillary ligand in organometallic chemistry for a variety of reasons. Thus, the M–Cp\* bond is very strong, and the Cp\* ligand rarely dissociates from the metal or takes part in any reaction. Its steric bulk confers kinetic stabilization upon complexes, and the methyl substituents ensure good solubility in organic solvent. Last but not least, Cp\*M derivatives tend to crystallize well, affording opportunities for X-ray diffraction studies. As described earlier,  $[\text{RCrCl}_2(\text{THF})_3]$  reacted with TiCp or NaCp (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ) to generate cyclopentadienyl ligated complexes<sup>14</sup>. We have extended this reaction to the pentamethylcyclopentadienyl derivatives, in order to take advantage of the stabilizing effect of the bulkier ligand. When Cp\*Li was added to a solution of  $\text{MeCrCl}_2(\text{THF})_3$ , the dinuclear complex  $[\text{Cp}^*\text{Cr}(\text{Me})(\mu\text{-Cl})]_2$  (**1a**) was produced in good yield. Conversely, we also found that treatment of  $\text{CrCl}_3(\text{THF})_3$  with one equivalent of Cp\*Li in THF – to yield  $[\text{Cp}^*\text{Cr}(\text{Cl})(\mu\text{-Cl})]_2$  (**2**) *in situ*, followed by addition of a lithium alkyl reagent, RLi (R = methyl, ethyl, phenyl, benzyl etc.) yielded dimeric alkyl complexes of the formula  $[\text{Cp}^*\text{Cr}(\text{R})\text{Cl}]_2$  (**1**) (R = Me, **1a**; R = Et, **1b**; R = Ph, **1c**; R = Bn, **1d**; R =  $\text{CH}_2\text{SiMe}_3$ , **1e**) (Scheme 1)<sup>15,16</sup>. In general, these complexes are purple crystalline solids, soluble in common organic solvents. They are thermally stable but decompose upon exposure to air and/or moisture. The alkyl dimers were reactive towards Lewis bases (L, e.g. py, bipy, dppe, dmpe,  $\text{PMe}_3$  and 3,5-lutidine) resulting in mononuclear chromium(III) half-sandwich complexes. A series of new neutral (**3**, **4**, **5**, **6**), anionic (**7**) or cationic (**8**) half-sandwich complexes of chromium(III) was synthesized from **1a–e** (refs 15, 17, 18). These chromium(III) alkyl compounds obviously do not obey the 18-electron rule and in general their most common valence electron count is 15. A few unsaturated derivatives have 13-electron configuration (e.g. mononuclear  $\text{Cp}^*\text{Cr}(\text{CH}_2\text{SiMe}_3)_2$ ) (ref. 16).

In our exploration of Cr(III) chemistry we also looked at a related class of Cr(II) organometallics<sup>19</sup>. Thus,  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})]_2$  (**9**), can be prepared by reduction of  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})\text{Cl}]_2$  (**2**) with  $\text{Li}[\text{HBEt}_3]$  – i.e. an obvious attempt at making a Cr(III) hydride – or, in hindsight, by reaction of  $\text{CrCl}_2$  with Cp\*Li. This dinuclear halide in turn can serve as a precursor for alkylation reactions, to yield dinuclear Cr(II) alkyls of the type  $[\text{Cp}^*\text{Cr}(\mu\text{-R})]_2$ , (**10**) (R = Me, **10a**; R = Et, **10b**; R =  $^n\text{Bu}$ , **10c**; R =  $\text{CH}_2\text{SiMe}_3$ , **10d**; R = Ph, **10e**; R =  $\text{CH}_2\text{Ph}$ , **10f**). One of the more interesting of these is the benzyl derivative  $[\text{Cp}^*\text{Cr}(\mu\text{-Bn})]_2$  (**10f**) (ref. 20). It was unstable in solution and slowly converted to  $[\text{Cp}^*\text{Cr}(\eta^1\text{-Bn})(\mu\text{-}\eta^3\text{:}\eta^6\text{-Bn})\text{CrCp}^*]$  (**11**) (Scheme 2); upon heating the latter rearranges one more time, to produce a third isomer, namely  $[(\text{Cp}^*\text{Cr})_2(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_5\text{-CH}_2\text{CH}_2\text{-C}_6\text{H}_5)]$ .

Reaction of  $[\text{Cp}''\text{Cr}(\mu\text{-Cl})]_2$  (**9a**, Cp'' =  $\eta^5$ -ethyl-tetramethylcyclopentadienyl) with  $\text{Li}[\text{HBEt}_3]$  rapidly gave



Scheme 1.



Scheme 2.

$[\text{Cp}^*_4\text{Cr}_4(\mu_3\text{-H})_4]$  (**12**) in 60% yield<sup>19</sup>. Exposure of **12** to hydrogen gas at high pressure yielded the mixed valent polyhydride cluster  $[\text{Cp}^*_4\text{Cr}_4\text{H}_7]$  (**13**). This compound was characterized by a single crystal X-ray diffraction and by a neutron-diffraction study<sup>21</sup>, to unambiguously ascertain the number of hydride ligands.

### Paramagnetic NMR

The principal difficulty in the investigation of paramagnetic organometallics lies in their NMR spectra. The presence of unpaired electrons in the same molecule results in large isotropic shifts (up to several hundred ppm) and severely broadened resonances, which usually obscure any nuclear spin-spin coupling and make integration of signals difficult. Nuclei bonded directly to the metal (e.g. hydrides), or even protons attached to carbon atoms directly bonded to Cr(III) (e.g. methyl groups) are typically unobservable. The magnitude of these effects depends on the number of unpaired electrons and the electron spin relaxation time, varying with the metal, formal oxidation state, and coordination environment<sup>22</sup>. In effect, there exists no generally applicable empirical relationship between chemical shift and chemical environment, and the line broadening can make signals of low intensity all but undetectable. That said, NMR spectra of paramagnetic compounds are easily acquired, simply by increasing the sweep width of the FT NMR spectrometer and rapidly pulsing away. No need to worry about saturation – the compounds have built in relaxation reagents!

When the line broadening becomes a serious obstacle, one can take advantage of a phenomenon that results in narrower lines. Specifically, substitution of  $^1\text{H}$  atoms with the  $^2\text{H}$  isotope coupled with  $^2\text{H}$  NMR spectroscopy results in spectral lines that are up to 40 times narrower than those of corresponding  $^1\text{H}$  NMR spectra, due to slower nuclear relaxation of the  $^2\text{H}$  nuclei in paramagnetic compounds<sup>23</sup>. One of the apparent disadvantages of this technique would seem to be the need for the preparation of selectively deuterium labelled compounds. However, with modern FT NMR equipment, the natural abundance of deuterium can be sufficient to take advantage of the line narrowing effect by recording  $^2\text{H}$  NMR spectra of unlabelled compounds<sup>24</sup>.

Isotope exchange experiments also revealed another peculiarity of the NMR spectra of paramagnetic compounds, namely the observation of extremely large isotope effects on chemical shifts (we have coined the acronym PIECS, i.e. Paramagnetic Isotope Effect on Chemical Shift, for this phenomenon). A particularly interesting case of this was observed in H/D exchange reactions of  $[\text{Cp}^*_4\text{Cr}_4(\mu_3\text{-H})_4]$ , yielding mixtures of isotopomers of the constitution  $[\text{Cp}^*_4\text{Cr}_4(\mu_3\text{-H})_n(\mu_3\text{-D})_{4-n}]$ <sup>25</sup>. The  $^{13}\text{C}$  NMR resonances of the cyclopentadienyl ring exhibited shifts of up to 3 ppm per incremental H/D substitution. Indeed, this phenomenon was used to unambiguously 'count' the

number of hydrides present in the cluster and to reveal dynamic process that exchanges them rapidly on the NMR time scale.

### Structure

As part of this project, in a very productive collaboration with A. Rheingold's group at the University of Delaware we have determined the crystal structures of a large number of molecules. Two generalizations can be made based on our growing structural database. First, paramagnetic compounds do not differ significantly in any structural aspect from comparable 18-electron compounds. For example, the Cp\*-ring is bound to the chromium in an entirely normal  $\eta^5$ -mode, and many of the compounds adopt the familiar 'three-legged piano stool' geometry. The bond distances and angles are within reasonable expectations. For this reason, no actual molecular structures and metric parameters will be reproduced here (except one); they are readily available in the published literature for those who desire more detail. Just as a representative example of a typical Cr<sup>III</sup> alkyl, Figure 1 depicts the molecular structure of Cp\*Cr(py)Me<sub>2</sub> (ref. 26). However, it bears mentioning that our work would have been entirely impossible without access to rapid structure determinations by X-ray diffraction. While structural organometallic chemistry is now seasoned enough to allow prediction of the structures of diamagnetic compounds based on their NMR spectra in most cases, the same cannot be said for paramagnets. As mentioned earlier, the NMR spectra of paramagnets do not provide direct evidence about chemical environment and structure. To this date, we often do not know what we have made until the crystal structure 'opens our eyes'. In this context the rapid advance in X-ray diffraction technology (e.g. CCD detectors, fast computers, etc.) is a great advantage, and an absolute requirement for working with paramagnetic organometallics.

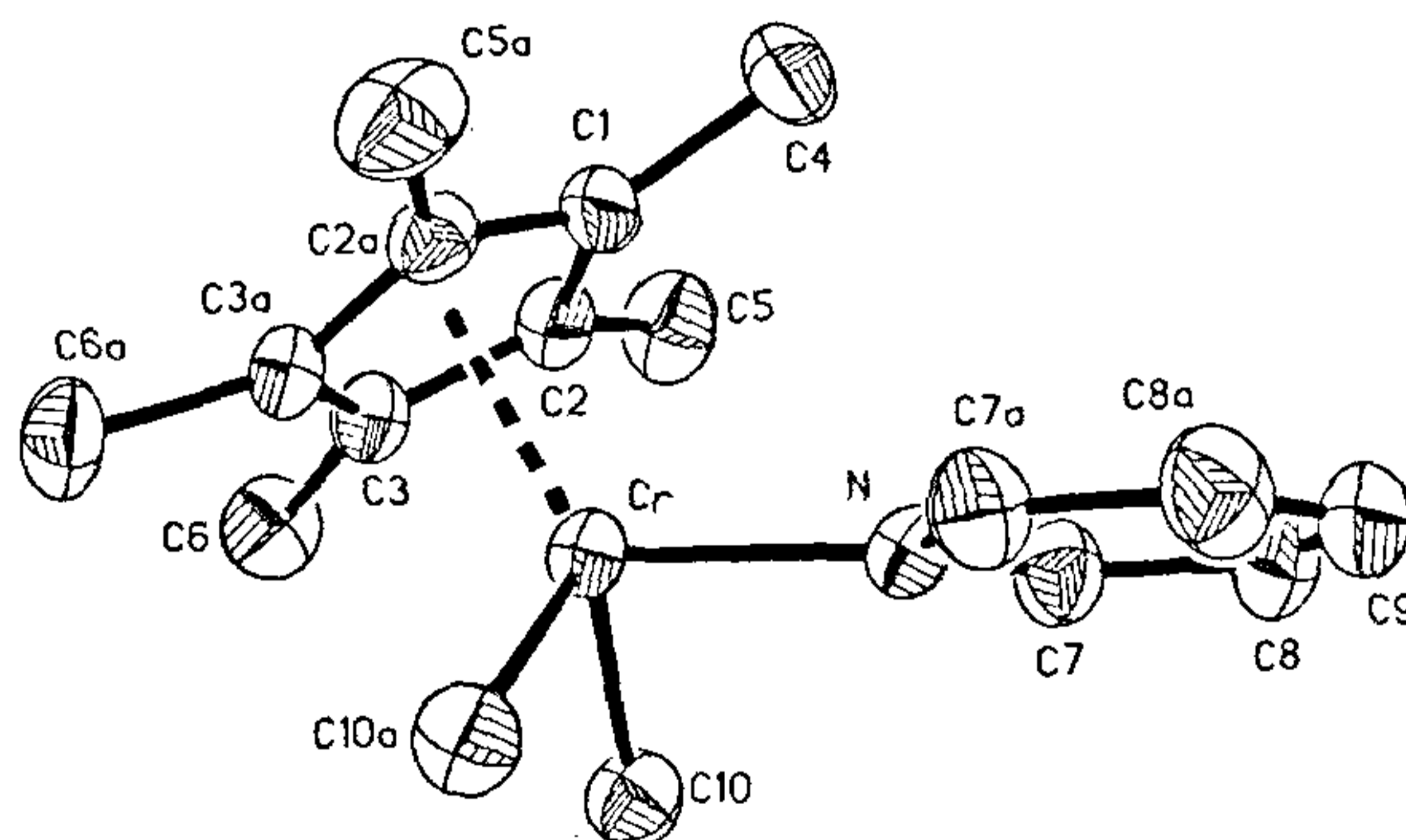


Figure 1. The molecular structure of Cp\*Cr(py)Me<sub>2</sub>; the molecule sits on a crystallographic mirror plane. Selected interatomic distances [Å]: Cr–C(Cp\*)<sub>avg</sub>, 2.28; Cr–C10, 2.091(5); Cr–N, 2.095(4) and angles [°]: C10–Cr–N, 93.7(1); C10–Cr–C10a, 96.3(34).

## Magnetism

Compounds with one or more unpaired electrons are paramagnetic, i.e. they exhibit a positive molar magnetic susceptibility ( $\chi_M$ ). The latter may be measured in using devices like Gouy or Faraday balances, SQUIDs, etc. or even by an NMR method (i.e. the Evans method) in solution. In 'magnetically dilute' compounds, i.e. those without significant interactions between spins, the magnetic susceptibility shows simple Curie-Weiss behaviour and an essentially temperature-independent effective magnetic moment ( $\mu_{\text{eff}}$ ). Thus, for mononuclear Cr(III) alkyls,  $\mu_{\text{eff}}$  will range between 3.8 and 4.0  $\mu_B$ , consistent with the spin-only moment of a system with three unpaired electrons ( $S = 3/2$ ). However, in cases where paramagnetic ions are very close together, or bridged by ligands, their spins may interact and this gives rise to various magnetic behaviours, depending on the nature of coupling between the individual magnetic moments. All of this is familiar to coordination chemists, but it rarely intrudes upon the turf of organometallic chemistry. Therefore some illustrative organometallic examples will be described in the following.

The dinuclear complexes  $[\text{Cp}^*\text{Cr}(\text{R})(\mu\text{-Cl})]_2$  and  $[\text{Cp}^*\text{Cr}(\text{Cl})(\mu\text{-Cl})]_2$  feature two pseudooctahedral Cr(III) ions joined by bridging chloride ligands into edge-sharing bioctahedra; the Cr-Cr distances of these molecules (ca. 3.3–3.5 Å) are too long to consider direct metal-metal bonding<sup>15</sup>. However, the magnetic moments of these molecules are smaller than 3.8  $\mu_B$  per Cr atom, and they decrease with temperature. As an example, the temperature dependence of the molar magnetic susceptibility and the effective magnetic moment of  $[\text{Cp}^*\text{Cr}(\text{Me})(\mu\text{-Cl})]_2$  (**1a**) is shown in Figure 2; these measurements are con-

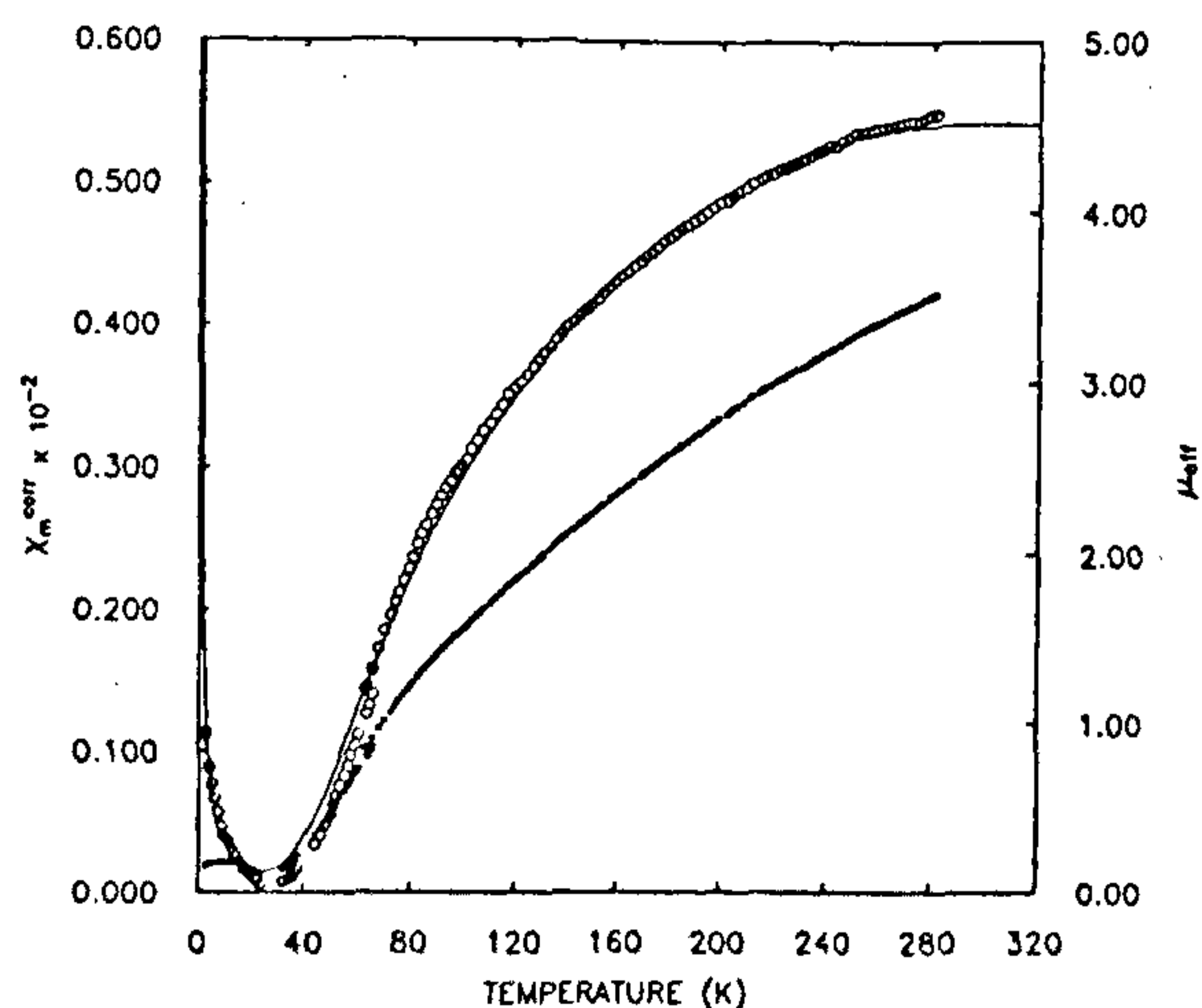


Figure 2. Temperature dependence of the molar magnetic susceptibility,  $\chi_M$  (O) and the effective magnetic moment  $\mu_{\text{eff}}$  (●) of  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})(\text{Me})]_2$  (**1a**).

sistent with antiferromagnetic coupling between the Cr atoms. Briefly summarized, the interaction between the metal atoms results in a splitting of the different possible spin states of the dinuclear complex, (i.e.  $S = 0, 1, 2, 3$ ), with the state of lowest multiplicity (here  $S = 0$ ) being the ground state. The latter is the defining criterion for antiferromagnetic coupling. A Boltzmann population of the closely spaced spin states results in the temperature dependence of  $\chi_M$  and  $\mu_{\text{eff}}$ ; these data can be used to derive a coupling constant  $J$  ( $J < 0$  for antiferromagnetic coupling), which serves as a measure of the magnitude of the interaction<sup>27</sup>. In this model,  $2J$  is the energy difference between the singlet ground state ( $S = 0$ ) and the first excited state ( $S = 1$ ). For **1a** this splitting is 240  $\text{cm}^{-1}$ , rather a small energy on the scale of chemical bonds.

While antiferromagnetic coupling is the rule for spin-spin interactions in polynuclear coordination compounds, occasionally one encounters ferromagnetic coupling; in this situation the spin state of highest multiplicity is the ground state of the manifold of possible spin states. An example of this behaviour was found for **11** (see Scheme 2). This molecule is most appropriately described as a mixed-valent Cr<sup>I</sup>/Cr<sup>III</sup> complex rather than being a dinuclear Cr<sup>II</sup> alkyl<sup>20</sup>. Figure 3 *a* depicts the temperature dependencies of  $\chi_M$  and  $\mu_{\text{eff}}$ . In contrast to the behaviour shown in Figure 2, the magnetic moment of **11** increases with decreasing temperature. The ground state of **11** has all spins coupled in a parallel fashion ( $S = 3/2$  for Cr(III) and  $S = 1/2$  for Cr(I)) resulting in a molecule with four unpaired electrons ( $S = 2$ ). The ferromagnetic interaction of chromium centres was confirmed by saturation magnetization measurements at low temperature (see Figure 3 *b*). The best fit obtained with a Brillouin function yielded three independent determinations of the spin quantum number  $S$  of the ground state, averaging to  $S = 2.08(12)$ .

One of the potential applications of organometallics with unpaired electrons is the design and assembly of molecular magnetic materials – i.e. bulk phases that exhibit cooperative magnetic properties on a larger scale<sup>28</sup>. In this context the preparation of molecules with high spin multiplicities is of interest. An example of such a molecule discovered as part of our project is the heptahydride cluster  $[\text{Cp}_4^*\text{Cr}_4\text{H}_7]$  (ref. 21). Its magnetic susceptibility showed no indication of either ferro- or antiferromagnetic coupling. Rather, the molecule behaved like an ordinary paramagnet, albeit with a magnetic moment consistent with seven unpaired electrons ( $S = 7/2$ ). Our interpretation of this observation is akin to a molecular version of ferrimagnetism. To wit,  $[\text{Cp}_4^*\text{Cr}_4\text{H}_7]$  is a mixed-valent compound with three Cr(III) ions ( $S = 3/2$ ) and one Cr(II) ion ( $S = 1$ ). Strong antiparallel alignment of each Cr(III) ion with the lone Cr(II) would thus align all three Cr(III) spin quartets in parallel ( $S = 9/2$ ), to be decreased to  $S = 7/2$  by antiparallel alignment with the Cr(II) triplet.

Magnetic interactions between open shell metal ions give rise to a plethora of fascinating and potentially useful

properties. Organometallic molecules may well play an important role in the design of novel magnetic materials. Such advances will not accrue from the study of diamagnetic 18-electron compounds, providing yet another impetus for the study of paramagnetic organometallics.

### Olefin polymerization

The coordination polymerization of small olefins such as ethylene and propylene is the most important industrial process involving organometallic intermediates<sup>29</sup>. Among the transition metals that catalyse the polymerization of olefins, chromium occupies a prominent position. Broadly speaking, two kinds of chromium-based polymerization catalysts are used commercially. The so-called 'Phillips catalyst' was discovered independently by Hogan and Banks at Phillips Petroleum Co in the late fifties; it is pre-

pared by deposition of inorganic chromium compounds on silica followed by calcination, leaving chromium in the hexavalent state<sup>30</sup>. Two decades later, Karapinka and Karol *et al.* at Union Carbide developed catalysts prepared by treatment of silica with low-valent organometallic complexes (notably chromocene,  $\text{Cp}_2\text{Cr}$ ) (ref. 31). The chemical nature of the active site(s), the formal oxidation state of the active species, and the mechanism of initiation of these chromium catalysts have been matters of wide ranging conjecture. It has been our belief that the study of organometallic compounds of chromium in solution can make an important contribution to the understanding and rational modification of heterogeneous catalysts. Thus, we set out to create a functioning homogeneous model system for the Union Carbide catalysts ( $\text{Cp}_2\text{Cr}/\text{SiO}_2$ ). As it turned out, the compounds required for this endeavour were all paramagnetic, containing Cr(III). The first active catalyst we discovered was the 15-electron complex  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{CH}_3]\text{BPh}_4$  (ref. 17). In  $\text{CH}_2\text{Cl}_2$  solution, this species exists in equilibrium with coordinatively unsaturated  $[\text{Cp}^*\text{Cr}(\text{THF})\text{CH}_3]^+$  via dissociation of a THF ligand. The 13-electron species is a good structural model of the proposed active site of the heterogeneous Union Carbide catalyst, and solutions of  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{CH}_3]\text{BPh}_4$  in  $\text{CH}_2\text{Cl}_2$  catalysed the polymerization of ethylene at ambient temperature and pressure without any added cocatalyst. Further investigations revealed that any coordinatively unsaturated  $\text{Cp}^*\text{Cr}(\text{III})$  alkyl, i.e. 13-electron complexes of the type  $\text{Cp}^*\text{Cr}(\text{X})\text{R}$  ( $\text{X} = \text{R}, \text{NR}_2, \text{OR}$ ) or  $[\text{Cp}^*\text{Cr}(\text{L})\text{R}]^+$  ( $\text{L} = \text{THF}, \text{Et}_2\text{O}, \text{etc.}$ ) proved catalytically active. However, in direct contradiction to the proposals prevalent in the literature, all Cr(II) alkyls were catalytically inactive. Therefore we have proposed that the active site of the Union Carbide catalysts is a Cr(III) alkyl<sup>32,33</sup>.

In addition to the fundamental scientific interest in the role of chromium in polymerization catalysis, there is also an applied component to our work. Compounds emerging from our laboratory are being evaluated for potential commercial application in collaboration with Chevron Chemical Co. Thus our work may eventually prove truly useful.

### Conclusions

It is now evident that research in organometallic chemistry must not be constrained by the narrow confines of the 18-electron rule and a restriction to diamagnetic compounds. While this rule provides some guidance for certain classes of organometallic compounds (notably low valent metal carbonyls), the field has advanced beyond these starting points. The exclusion of paramagnetic compounds is wholly arbitrary, and mostly motivated by experimental convenience. However, in our search for better catalysts, novel synthetic reagents, and advanced materials we cannot afford to ignore whole classes of com-

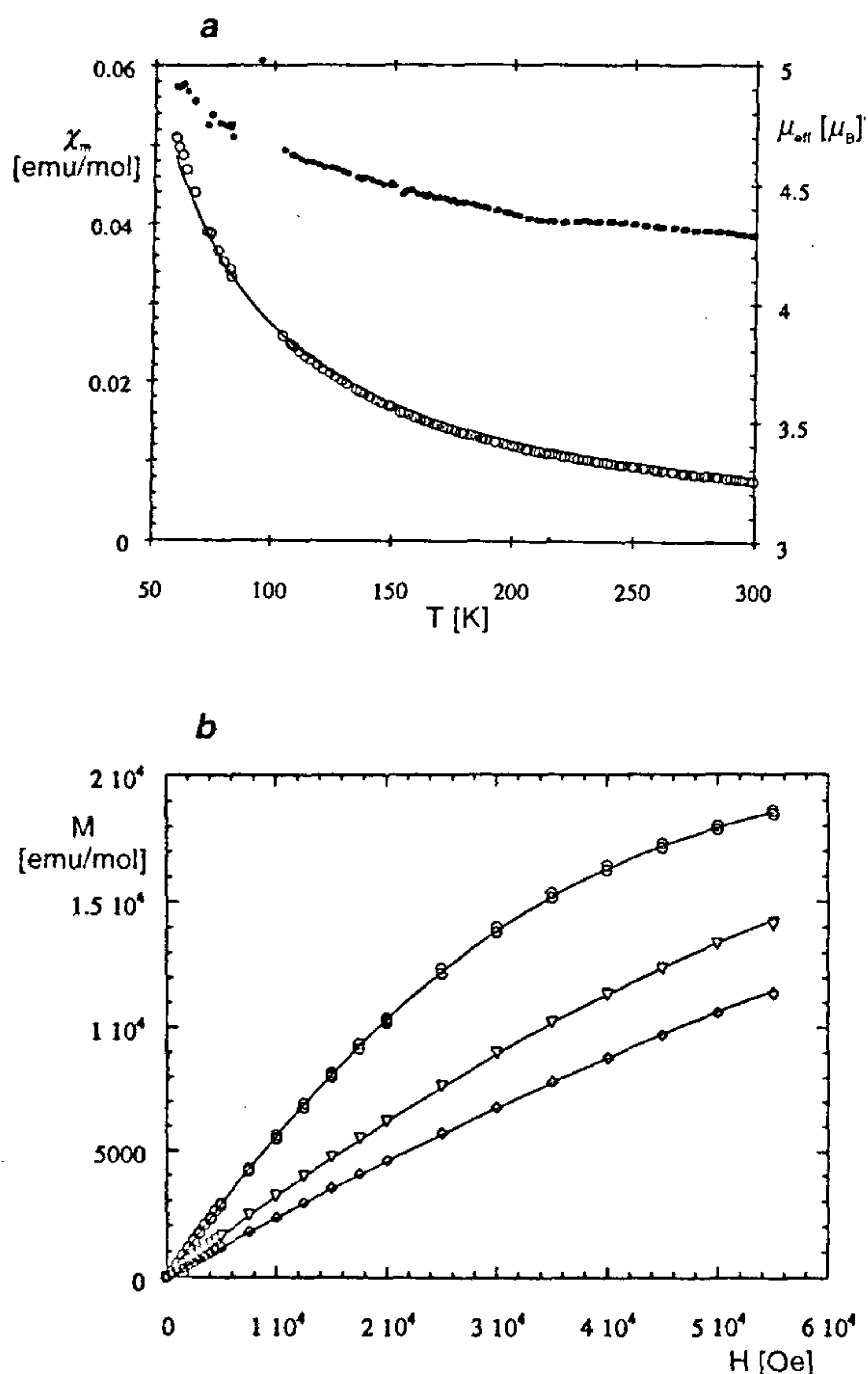


Figure 3. *a*, Temperature dependence of the molar magnetic susceptibility,  $\chi_m$  (O) and the effective magnetic moment  $\mu_{\text{eff}}$  (●) of  $[\text{Cp}^*\text{Cr}(\eta^1\text{-Bn})(\mu\text{-}\eta^3:\eta^6\text{-Bn})\text{CrCp}^*]$  (11); *b*, Saturation magnetization measurements for 11 at 5 K (O), 10 K (∇) and 15 K (◇) fit with Brillouin functions.

pounds. Due to the historical neglect of open shell organometallics the field beckons exploration. Many discoveries are yet to be made, and explorers who venture into this uncharted territory will be richly rewarded.

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