2570 *Organometallics* 1989, *8*, 2570–2577

Synthesis and Reaction Chemistry of a New Class of Paramagnetic Chromium(III) Alkyls. Characterization of Complexes Formed by Insertion of Nitriles into the Chromium–Carbon Bond

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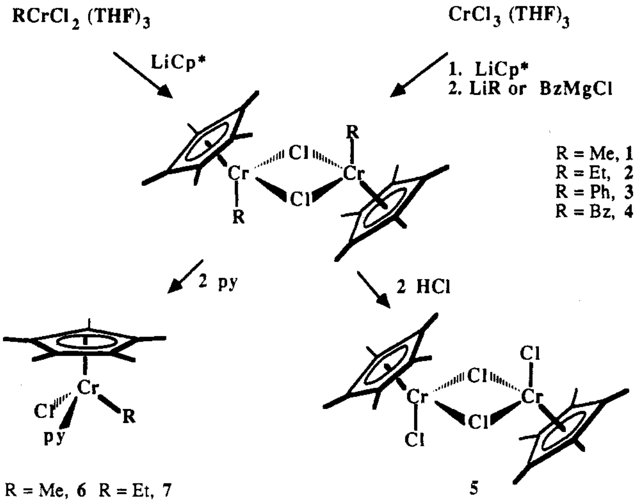
Received September 6, 1988; Revised Manuscript Received June 16, 1989

A series of dimeric chromium(III) alkyls $[(\eta^5\text{-}C_5Me_5)Cr(\mu\text{-}Cl)R]_2$ (R = Me, Et, Ph, Bz) has been prepared. Magnetic susceptibility measurements indicated antiferromagnetic coupling between the chromium centers. The chromium alkyls react with an excess of nitrile to form mononuclear β-diketimino complexes by insertion of nitrile into the chromium–carbon bond. With stoichiometric amounts of nitrile, dinuclear chromium complexes featuring bridging ketimino ligands are formed. The product from the reaction of $[(\eta^5\text{-}C_5Me_5)Cr(\mu\text{-}Cl)Me]_2$ with benzonitrile has been characterized by a preliminary X-ray structure determination. $[(\eta^5\text{-}C_5Me_5)Cr(\mu\text{-}Cl)Me]_2$ also reacts with 2-butyne to yield poly-2-butyne and the chromium(I) sandwich complex $[(\eta^5\text{-}C_5Me_5)Cr(\eta^6\text{-}C_6Me_6)]$. This 17-electron species exhibits both a reversible oxidation and reduction in THF.

Introduction

The elucidation of the chemical processes underlying catalysis remains a major challenge for chemistry in the years ahead.[1] A large fraction of catalytic reactions involves the interaction of organic molecules with transition metals, and consequently the organometallic chemistry of these elements has been a fertile area of study.[2] The historical development of this field is marked by a heavy emphasis on the synthesis and characterization of closed-shell molecules. A quick survey of the relevant literature reveals a plethora of diamagnetic compounds with 18-electron configurations—an attribute which has come to signify the organometallic "island of stability".[3] Recently, however, appreciation has been growing for the importance of radical reactions and reaction intermediates with 15; 17; or 19-electron configurations.[4] Obvious reasons for the historical bias against "metallaradicals" (paramagnetic organometallics) are the relative ease of preparation and handling of closed-shell molecules as well as the extraordinary importance of NMR spectroscopy as a means of characterization. However, evidence is mounting that metallaradicals display high and unusual reactivity and are thus particularly deserving of study.

Scheme I



We have initiated a study of the reactivity of paramagnetic chromium alkyls. Whereas the coordination chemistry of trivalent chromium has been the subject of much experimental work dating all the way back to Alfred Werner, organometallic compounds of chromium in the +III oxidation state are scarce by comparison.[5] The d^3 electronic configuration of Cr(III) ensures paramagnetism of such complexes. We began this work with the anticipation that an exploration of the reaction chemistry of chromium(III) alkyls might lead to the discovery of novel chemistry. Herein we report the synthesis and characterization of a new class of chromium alkyl complexes and their reactions with nitriles and alkynes.

Results and Discussion

Synthesis of Chromium Alkyls. As described earlier,[6] chromium alkyls of the type $RCrCl_2(THF)_3$[7] react with TlCp or NaCp (Cp = C_5H_5, cyclopentadienyl) to generate cyclopentadienyl ligated complexes. We have now extended this reaction to the pentamethylcyclopentadienyl ligand (C_5Me_5, Cp*) in order to take advantage of the stabilizing effect of this bulky ligand. For example, when LiCp* was added to a THF solution of $MeCrCl_2(THF)_3$ at room temperature, an immediate color change from light green to a dark purple indicated reaction. Evaporation of solvent, extraction with toluene, and recrystallization

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[1] Pimentel, G. C. *Opportunities in Chemistry*; National Research Council, 1985.

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[5] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1980; p 731. (b) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds., Pergamon Press: Oxford, 1982; Vol. 3. (c) Espenson, J. H. *Prog. Inorg. Chem.* **1983**, *30*, 189.

[6] Richeson, D. S.; Hsu, S.-W.; Fredd, N. H.; Van Duyne, G.; Theopold, K. H. *J. Am. Chem. Soc.* **1986**, *108*, 8273.

[7] (a) Nishimura, K.; Kuribayashi, H.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1972**, *37*, 317. (b) Kurras, E. *Naturwissenschaften* **1959**, *46*, 171.

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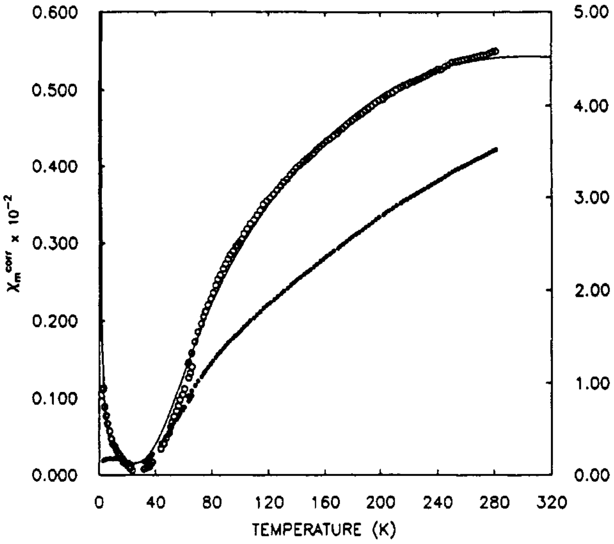

Figure 1. Temperature dependence of the corrected molar susceptibility, χ_m^{corr} (open circles), μ_{eff} (solid circles), and the fit to eq 4.

from toluene/pentane yielded dark purple crystals of a new material. Analytical and spectroscopic characterization of this material were consistent with structure 1 (Scheme I), a chromium dimer in which the two metal atoms are bridged by two chloride ligands. This structure assignment was based on the similarity in both physical properties and reactivity between 1 and its Cp analogue $[CpCr(Me)Cl]_2$, which has been structurally characterized by X-ray diffraction.[6] Complex 1 was isolated in 77% yield based on $MeCrCl_2(THF)_3$. It decomposed rapidly upon exposure to air.

Similar reactions yielded related complexes containing ethyl and phenyl substituents bonded to chromium. However, the limited availability and stability of suitable precursors of the type $RCrCl_2(THF)_3$ led us to search for an alternate and more general route to alkyl dimers related to 1. We have found that treatment of $CrCl_3(THF)_3$ with LiCp* in THF followed by addition of the appropriate alkyllithium or Grignard reagent to the intermediate generated in situ provided a convenient preparation of all the dimers described herein (Scheme I).

Treatment of 1 in THF with a slight excess (3.0 equiv) of gaseous HCl immediately yielded methane and a blue-green solution. From this solution was isolated the chloride dimer $[Cp^*CrCl_2]_2$ (**5**) in 83% yield. The Cp analogue of this molecule (i.e. $[CpCrCl_2]_2$) has been structurally characterized by Koehler et al.,[8] and our assignment of a dimeric structure to **5** rests on the similarity of these two compounds with respect to their physical properties.

The alkyl dimers were rapidly cleaved by Lewis bases, resulting in mononuclear half-sandwich complexes of chromium(III). For example, addition of pyridine to 1 and 2 respectively yielded the corresponding substituted derivatives 6 and 7 (Scheme I). We have previously prepared a more extensive series of such derivatives in the related Cp system,[6] and the synthesis of these two compounds indicates that the tendency of the alkyl dimers to add nucleophiles carries over to the Cp*-substituted molecules.

Magnetism. Dimers 1–5 contain two pseudooctahedral Cr(III) ions held in close proximity (the chromium–chromium distance in $[CpCr(Me)Cl]_2$ is 3.287 Å) by bridging chloride ligands. The interaction between the two metal atoms is not strong enough to form a metal–metal bond. However, magnetic susceptibility measurements indicated that the chromium ions were antiferromagnetically coupled through the bridging atoms. Figure 1 shows the results of such measurements on 1. The effective magnetic moment (μ_{eff}) of 1 is seen to be temperature dependent. At very low temperatures the molecule is nearly diamagnetic whereas the high temperature moment (3.5 μ_B at 280 K) corresponds to an average of approximately three unpaired electrons per dimer. This behavior is due to intramolecular coupling of the spins of the unpaired d electrons.[9] Application of the Heisenberg–Dirac–Van Vleck (HDVV) model, including both bilinear and biquadratic terms for this coupling interaction, to the case of two coupled $S = {}^3/_2$ atoms yields a manifold of spin states (see Scheme II) characterized by energy spacings which are functions of both J and j. Antiferromagnetic coupling by definition assigns the state of lowest multiplicity (here $S = 0$) to the ground state. Hence the compound is diamagnetic at very low temperature. However, upon raising the temperature, higher spin states are populated in a Boltzmann distribution and the resulting temperature-dependent spin equilibrium results in the increase in magnetic moment. Fitting of the magnetic susceptibility data to an appropriate expression (see Experimental Section) allows the determination of the coupling constant J and j. This in turn permits the calculation of the singlet–triplet energy spacing, ΔE. There exists an extensive body of data on magnetically coupled polynuclear transition-metal complexes and attempts to correlate J values with structural variations.[10] Table I lists the coupling constants obtained

Scheme II

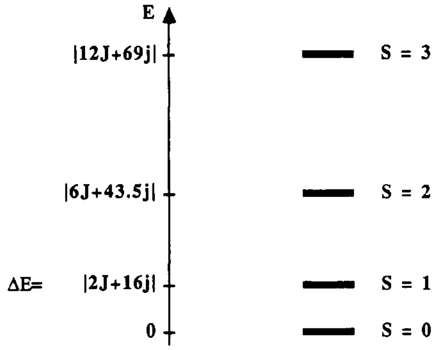

Table I. Values of Effective Magnetic Moment at a Given Temperature, Bilinear and Biquadratic Exchange Constants (See Eq 2), and the Calculated Singlet–Triplet Energy Spacing, ΔE (See Scheme II)

compd	μ_{eff}, μ_B (T, K)	−45	j, cm^{-1}	ΔE, cm^{-1}
1	3.5 (280	−45	9.3	240
2	3.9 (298)			150[a]
3	4.2 (296)			150[a]
4	4.6 (298)	−45	0.69	101
5	4.7 (298)	−24	3.6	107
11	4.0 (293)			150[a]
12	4.6 (299)			100[a]
13	4.1 (300)	−44	4.0	154

[a] Estimated from μ_{eff} (T)

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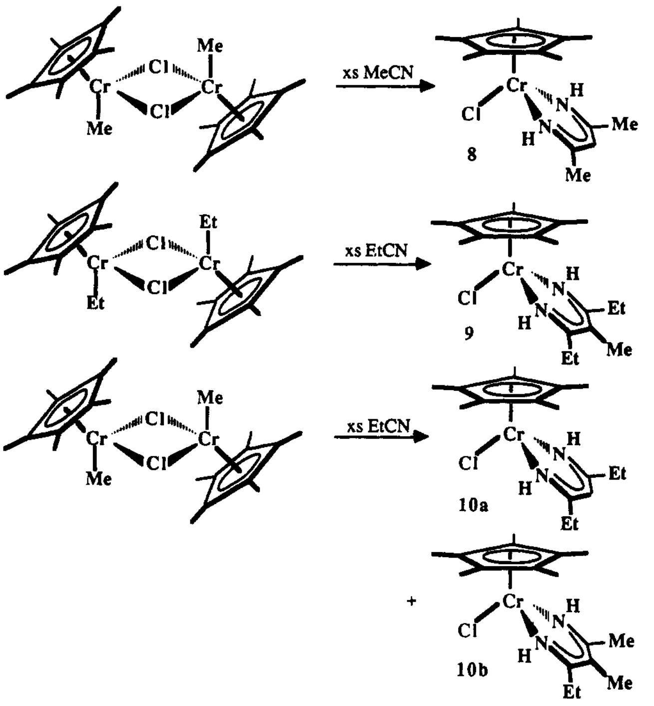
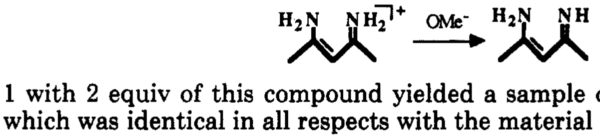
Scheme III



by fitting the susceptibility data obtained for compounds 1, 4, and 5.

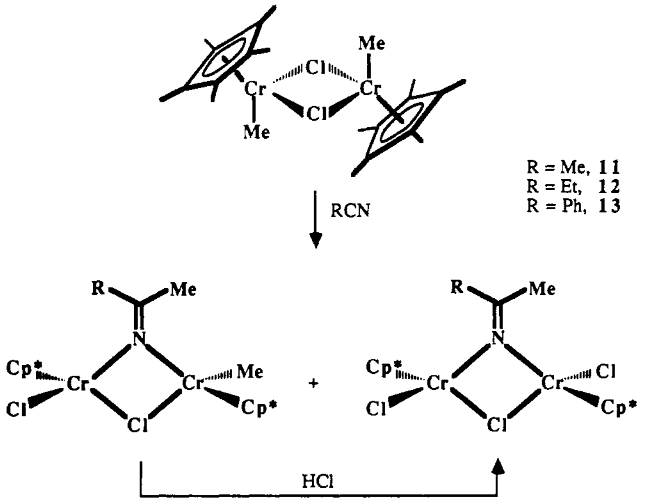
Reaction with Nitriles. The dimeric chromium alkyls described above feature chromium in a 15-electron configuration. This degree of electronic unsaturation combined with the facility of binding of external ligands should render the molecules highly reactive. Indeed, we have found that the dimers react at room temperature with nitriles, a class of molecules not generally thought to be very reactive toward transition-metal alkyls. When an excess of acetonitrile was added to a toluene solution of 1, the color of the solution changed from purple to brown. From this solution could be isolated a brick red microcrystalline solid. A strong band at 3261 cm^{-1} in the IR spectrum of this material was assigned to an N–H stretching vibration. Analytical and spectroscopic characterization of this compound were consistent with structure 8 (Scheme III), a mononuclear chromium complex with a bidentate ligand incorporating the methyl group originally bound to the metal as well as two molecules of acetonitrile. Despite prolonged attempts we were unable to produce X-ray quality crystals of 8 or one of its analogues. Thus we decided to synthesize 8 in an independent and more direct fashion to confirm its structure. Acetylacetone was converted into the β-diketimine following the procedure of McGeachin (eq 1).[11] Reaction of



(1)

1 with 2 equiv of this compound yielded a sample of 8 which was identical in all respects with the material isolated from the reaction of 1 and MeCN. In an attempt to trace the origin of the nitrogen-bound protons of 8, methyl dimer 1 was allowed to react with CD_3CN. The IR spectrum of the product of this reaction exhibited a strong band at 2420 cm^{-1}, consistent with an N–D stretching vibration. At the same time the N–H band at 3261 cm^{-1} had disappeared almost completely (assuming equal extinction coefficients for the two absorptions about 8% of the nitrogens were bonded to H).

Scheme IV



Reaction of ethyl dimer 2 with an excess of propionitrile yielded the expected symmetric product 9. However, addition of an excess of propionitrile to 1 apparently gave a mixture of two compounds. The ^1H NMR spectrum of the material obtained from this reaction was consistent with the presence of two isomers (**10a,b**) in a 3:2 ratio.

The formation of the β-diketimino complexes 8, 9, and **10a,b** required an excess of nitrile. When near stoichiometric amounts of nitriles were used, another set of products was formed. When 1 was allowed to react with 2.0 equiv of acetonitrile, propionitrile, or benzonitrile, respectively, blue crystalline products were isolated in each case. The IR spectra of these complexes did not show N—H stretches, but they did exhibit absorptions attributable to C=N bonds. The structure of these materials remained obscure for some time because their analytical data could not be reconciled with any reasonable composition. Ultimately the products of these reactions were shown to be mixtures of compounds related by replacement of an alkyl ligand with chloride (Scheme IV). Treatment of these mixtures with gaseous HCl liberated nonstoichiometric amounts of methane and yielded homogeneous samples of empirical composition $Cp^*{}_2Cr_2Cl_3(NC(Me)R)$ in each case.

Structure. In order to determine the nature of the blue products the crystal structure of the benzonitrile derivative 13 was determined by X-ray diffraction. The use of Cu Kα radiation and our failure to apply an absorption correction to the data rendered the numerical results of this determination suspect ($R = 0.082$, $R_w = 0.128$), but the chemical connectivity is clearly established and is shown in Figure 2 (see supplementary material for tables of positional parameters and selected distances and angles). The structure consists of well-separated molecules of 13. Each molecule is a binuclear complex containing two Cp*CrCl fragments held together by a bridging chloride and a μ_2-ketimino ligand. The two Cp* ligands are situated in a trans arrangement. The chromium–chromium distance is longer than 3 Å, consistent with the absence of a direct metal–metal bond. This was also supported by magnetic susceptibility measurements, which showed antiferromagnetic coupling of the chromium ions in compounds 11–13 (see Table I).

Compound 13 is one of a small number of structurally characterized complexes containing a ketimino ligand

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[11] McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903.

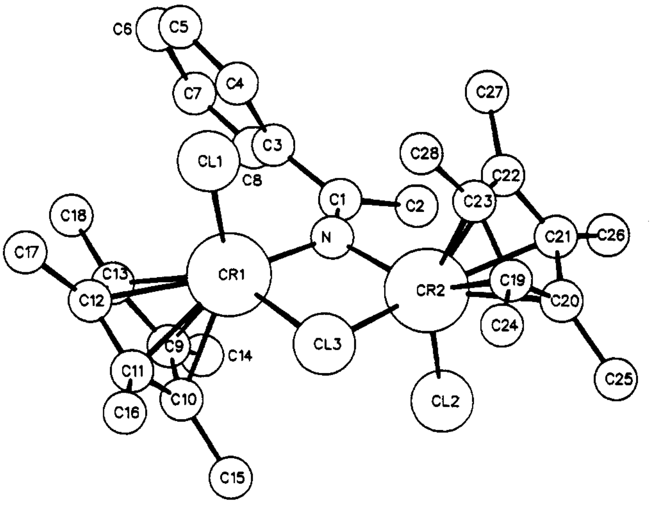
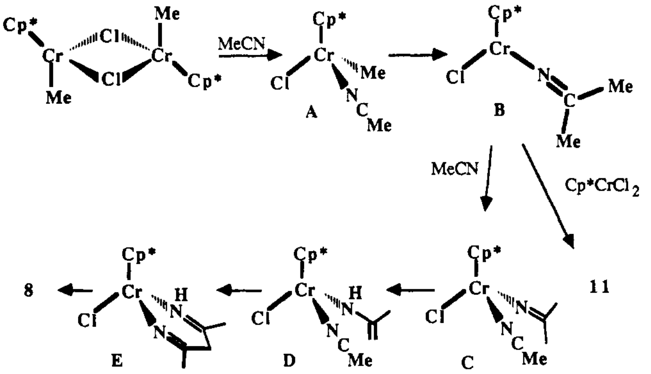


Figure 2. Molecular structure of **13**.

Scheme V



bridging between two transition metals, the other examples being $(\mu_2\text{-}Ph_2C{=}N)_2Fe_2(CO)_6$[12] and $(\mu_2\text{-}(CF_3)_2C{=}N)\text{-}Mn_2(CO)_7$.[13] The whole ketimino ligand is distorted somewhat to avoid a severe steric interaction of the phenyl ring with the Cp* ring on Cr1.

Mechanism. There are only a few reports available on insertions of nitriles into transition-metal alkyls.[14] All of these involve highly Lewis acidic early transition elements of f-block metals. Coordination of the nitrile to the metal activates it toward nucleophilic attack by the rather negatively polarized alkyl ligand. Scheme V depicts a proposed mechanism for the formation of the various products described above. Cleavage of the dimer by added nitrile yields a mononuclear complex akin to the pyridine adducts **6** and **7**. However, this molecule can react on by undergoing a migratory insertion of nitrile into the chromium–alkyl bond, thus yielding a coordinatively unsaturated ketimino complex (B). When the reaction is run at low nitrile concentration, B is stabilized by association of another metal fragment. Both Cp*Cr(R)Cl (available from cleavage of the starting material) and Cp^*CrCl_2 (which is presumably generated in a metathetical alkyl/chloride exchange) may serve in the role of the trapping agent, thus explaining the formation of mixtures of compounds (see above). In the presence of an excess of nitrile, B is rapidly trapped by the organic ligand forming coordinatively saturated species C. In preparation for the formation of the carbon–carbon bond to the second nitrile the ketimino ligand must then undergo a tautomerization to the enamine form (D). The outcome of the labeling experiment with CD_3CN (see above) raises the possibility of regioselectivity in this step. One possible interpretation of the nearly exclusive formation of N–D containing **8** would call for a regioselective tautomerization favoring the shift of hydrogen (deuterium in the labeling experiment) from the nitrile-bound methyl group. We note that the two methyl groups of the ketimino ligand in the corresponding static intermediate C can never be equivalent, due to the low symmetry (C_1) of the molecule. Rotation around the Cr–N bond would of course equilibrate the two methyl groups. However, an observation that militates strongly against this interpretation is the formation of two isomers of **10** in the reaction of **1** with propionitrile. The two compounds are presumably formed via two isomeric intermediates of type D, which in turn result from tautomerization of an unsymmetrical ketimino complex. The observed product ratio (**10a**:**10b** = 3:2) directly reflects the ratio of available α-hydrogens in the B-type intermediate. Thus there must be another explanation for the large N–D/N–H ratio of **8** produced in the CD_3CN reaction. Reasoning that this large ratio could be the result of exchange of initially formed N–H groups with the deuterium pool in the excess CD_3CN, we checked whether **8** would undergo such an exchange. Dissolution of **8** in CD_3CN and inspection of the IR spectrum of material reisolated after 24 h showed no evidence of any exchange. Even the addition of a small amount of the strong base lithium tetramethylpiperidide did not change this outcome. As a final test of the possibility of exchange, **8** was submitted to the reaction conditions of its formation; a mixture of **8**, CD_3CN, and ethyl dimer **2** was allowed to react, and the products of this reaction were examined by mass spectrometry. The mass spectrum of the product mixture indicated that there had been incorporation of deuterium into **8** resulting in a mixture of species with a $8\text{-}d_0{:}8\text{-}d_1{:}8\text{-}d_2$ ratio of approximately 6:5:1. We also examined the mass spectrum of **8** produced by reaction of **1** with CD_3CN. The spectrum was consistent with the presence of a mixture of $8\text{-}d_6$ (52%), $8\text{-}d_7$ (11%), $8\text{-}d_8$ (21%), and $8\text{-}d_9$ (16%). Whereas $8\text{-}d_6$ is simply formed by incorporation of two molecules of CD_3CN, the other species must result from exchange of one to three protons originating on the methyl group bound to chromium. Likely candidates for this exchange are postulated intermediates C and D, which may interconvert reversibly. Returning to Scheme V, nucleophilic attack of the enamine of D on the coordinated acetonitrile closes the heterocyclic ring and yet another tautomerization yields the final product.

Reaction with Alkyne. Given the facile reaction of the dimeric chromium alkyls with the carbon–nitrogen triple bond, we decided to explore their reactions with the carbon–carbon triple bond, i.e. alkynes. Heating of a mixture of **1** and a large excess (40 equiv) of 2-butyne in toluene to 60 °C for 3 days produced a color change from purple to dark green and the precipitation of a colorless solid. The solid was identified as poly-2-butyne by its spectroscopic properties.[15] From the solution two organometallic

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[12] Bright, D.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1967**, 245.

[13] Churchill, M. R.; Lin, K. K. *Inorg. Chem.* **1975**, *14*, 1675.

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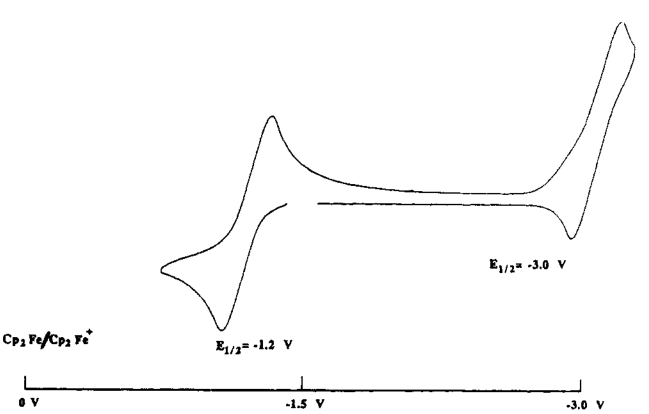
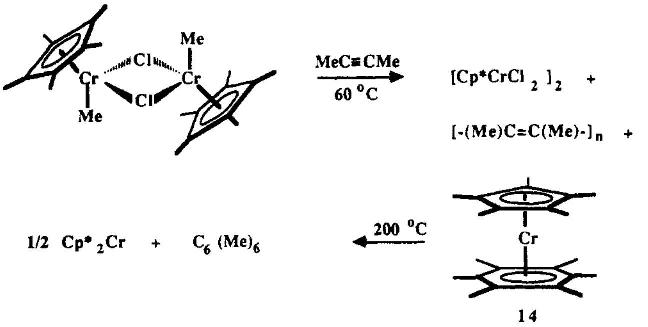


Figure 3. Cyclic voltammogram of 14 in THF (referenced to Cp_2Fe/Cp_2Fe^+, scan rate = 100 mV/s).

Scheme VI



products were isolated. One was the chloride dimer **5**, and the other was a new compound that formed orange crystals upon cooling of a pentane solution. Analytical and spectroscopic data for this compound were consistent with structure **14** (Scheme VI), a new sandwich complex of chromium in the +I oxidation state. The magnetic susceptibility of **14** was measured; μ_{eff} at room temperature was 1.9 μ_B, consistent with one unpaired electron. **14** proved to be quite robust. Heating a solution of it in C_6D_6 to 200 °C over several days eventually produced a mixture of $Cp^*{}_2Cr$ and hexamethylbenzene. An electrochemical investigation of **14**, a 17-electron complex, revealed a reversible oxidation at $E_{1/2} = -1.2$V vs ferrocene (see Figure 3). The reduction of **14**, to yield a 18-electron species, is centered at -3.0 V and appears to be electrochemically reversible ($\Delta E_p = 0.25$ V, $\Delta E_p(Cp_2Fe/Cp_2Fe^+) = 0.29$ V); however, the ratio of the peak currents (i_{pc}/i_{pa}) is only about 0.75. This observation may be attributed to the onset of irreversible solvent reduction occurring at -3 V.

Conclusions. We have prepared a novel class of paramagnetic alkyl complexes of chromium(III). The compounds are dimers held together by bridging chloride ligands, and the chromium atoms are antiferromagnetically coupled. The 15-electron configuration of the chromium atoms renders them electronically unsaturated and highly Lewis acidic. As a result of their nature the compounds easily add external nucleophiles and undergo rapid insertion reactions with unsaturated organic molecules. The reaction with nitriles has been studied in some detail. Depending on the substrate concentration one or two nitrile molecules are incorporated, resulting in the formation of μ_2-ketimino or β-diketimino complexes. This study shows that organometallic complexes of chromium(III) have unique and interesting chemistry. As part of our study of metallaradicals in general we are continuing our exploration of the reactivity of alkyls in this neglected oxidation state.

Experimental Section

General Considerations. All manipulations of compounds and solvents was by standard Schlenk, vacuum, and glovebox techniques. Pentane, diethyl ether, tetrahydrofuran and toluene were distilled from purple Na benzophenone/ketyl solutions. Acetonitrile, propionitrile and benzonitrile were distilled from P_2O_5 and stored under N_2. Pyridine was distilled from BaO and stored under nitrogen. Benzene-d_6 was distilled from Na/K alloy. HCl (tech) was purchased from Matheson Gas Co. and used without further treatment. $CrCl_3$ (anhydrous), $C_6H_5CH_2MgCl$ (in Et_2O), CH_3Li (in Et_2O), PhLi (in cyclohexane/Et_2O), and ^{n}BuLi (in hexanes) were purchased from Aldrich Chemical Co. and used without further purification. LiCp* was synthesized by the literature procedure.[16] 4-Amino-2-imino-3-pentene was synthesized by the literature procedure[11] with the following modification; in the deprotonation of 4-amino-3-penten-2-imonium tetrafluoroborate to generate the free base, ^{n}BuLi was used rather than a solution of $NaOCH_3$ in CH_3OH.

^{1}H NMR spectra were taken on a Bruker WM-300 spectrometer and were referenced to the residual protons of benzene-d_6 (δ 7.15).[17] FTIR spectra were taken on an Mattson Alpha Centauri spectrometer with a resolution of 2 cm^{-1}. KBr pellets were prepared in a drybox. CI and FAB mass spectra were obtained with A.E.I. MS 902 and Kratos MS890 mass spectrometers, respectively. Melting points were measured on a Mel-Temp melting point apparatus and are uncorrected.

Electrochemical measurements were done with a BAS CV-27 potentiostat using a Pt disk working electrode, a Ag counter electrode, and a Ag/AgCl,Me_4NCl (THF) reference electrode. This reference electrode consisted of a glass electrode body with cracked bead filled with a saturated solution of AgCl and Me_4NCl in THF in contact with a Ag wire. Typical substrate and supporting electrolyte ($^nBu_4NBF_4$) concentrations were 1 and 100 mM, respectively. Potentials are referenced to Cp_2Fe/Cp_2Fe^+ which has a potential of 0.82 V vs this reference electrode. All electrochemistry was done under inert atmosphere in a Vacuum Atmospheres drybox.

Elemental analyses were performed by Chemical Analytical Services at the University of California at Berkeley.

Magnetic Measurements and Data Fitting. Magnetic measurements were performed by using the Faraday method with $HgCo(SCN)_4$ as a calibrant (16.44 × 10^{-6} emu/g at 298 K). Temperature was varied by use of a He flow cryostat. All samples were polycrystalline and were loaded into high purity quartz buckets in a drybox. Samples were transferred by using an O-ring sealed container. Variable-field measurements (100 and 70% field strength) were done on all samples to check for ferromagnetic impurities. All measurements are corrected for the susceptibility of the bucket and for sample diamagnetic by using standard Pascal constants.[19]

Fitting of the susceptibility versus temperature data was done on the Chemistry Research Computing Facility, Prime 9950 computer. Exchange coupling in the dinuclear complexes was described by the Hamiltonian[20]

$$\mathcal{H} = -2J(S_1S_2) - j(S_1S_2)^2 \qquad (2)$$

where J is the bilinear exchange constant between the metal centers, j is the biquadratic exchange constant, and S_1 and S_2 are the spin vectors of the atoms, which in the case of Cr(III) have a magnitude of $^3/_2$. Application of the Van Vleck equation[21] results in the following expression for the susceptibility

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(16) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *137*, 1.

(17) The broad resonances characteristic of paramagnetic compounds make integration difficult; therefore, the integrals obtained were not always of the correct or integral ratios. Therefore, assignments were not always clear and those given are based on comparisons of a given compound with those of the same class.

(18) The TIP values, obtained from the least-squares fit, for many of the binuclear complexes seemed anomalously high. It is possible that the inadequacies of the simple HDVV model introduce an error into this fitting parameter.

(19) Hellwege, K.-H., Hellwege, A. M., Eds. *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Landolt-Bornstein Series*; Springer-Verlag: Berlin, 1981; Vol. 11.

(20) Griffith, J. S. *Struct. Bonding (Berlin)* **1972**, *10*, 87.

(21) Van Vleck, J. H., Ed. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: London, 1932.

$$\chi = \frac{N\mu_B^2 g^2}{3kT}\left(\frac{6e^{(-2J+16.5j)/kT} + 30e^{(-6J+43.5j)/kT} + 84e^{(-12J+69j)/kT}}{1 + 3e^{(-2J+16.5j)/kT} + 5e^{(-6J+43.5j)/kT} + 7e^{(-12J+69j)/kT}}\right) \quad (3)$$

where g is the gyromagnetic ratio (fixed at 2.0), μ_B is the Bohr magneton, and k is the Boltzmann constant. In order to correct for the possibility of a small amount of an $S = {}^3/_2$ impurity which would cause a Curie tail at low temperatures and to allow for the possibility of temperature-independent paramagnetism[9b] (TIP), the equation used in the fitting of the bimetallic complexes was

$$\chi_m = (Ng^2\mu_B^2 S(S+1)/3kT)P + (1-P)\chi + \chi_0 \quad (4)$$

where P is the mole fraction for an impurity, χ_0 is the value of the TIP, and χ is given by eq 3.[18]

For the monomeric complexes, fitting was done with a Curie–Weiss expression[9b]

$$\chi_m = C/(T - \Theta) + \chi_0 \quad (5)$$

where χ_0 is once again the TIP and Θ is the Weiss constant.

X-ray Structure Determination of 11. Crystals of 11 were obtained by cooling a concentrated ether solution to −30 °C. A crystal was sealed in a glass capillary under nitrogen. The chromium and chlorine atomic positions were determined by MULTAN. All other non-hydrogen atoms were located by subsequent difference Fourier maps. The program CRYSTALS was used for the block-diagonalized least-squares anisotropic refinement of all non-hydrogen atoms using both real and imaginary contributions to the atomic scattering factors. This refinement converged to a standard R of 0.082 (R_w = 0.128) for 3116 observed reflections. Hydrogen atomic positions were generated from assumed geometries and were not refined. The hydrogen isotropic temperature factors used were 1.2 times that of the attached carbon. There were no corrections made for absorption due to the poor crystal morphology. The intensity of the three standard reflections remained essentially constant during the experiment; therefore, no decomposition correction was applied.

Syntheses of Bis(μ-chloro)dimethylbis(η^5-pentamethylcyclopentadienyl)dichromium(III) {(Cp*CrMeCl)$_2$} (1). Method A. To a THF solution of $MeCrCl_2 \cdot 3THF$[7a] (4.27 g, 12.1 mmoles) was added 1 equiv of LiCp* (1.73 g, 12.2 mmol) all at once. This addition was followed by an immediate color change from green to dark purple. After the solution was allowed to stir for about 1 h, the solvent was evaporated to dryness. The resulting solid was extracted with toluene to yield an insoluble white solid (presumably LiCl, 0.62 g) and a dark purple solution. Addition of pentane and cooling to −30 °C yielded dark purple crystals (2.21 g) in 1 in 77% yield. **Method B.** $CrCl_3 \cdot 3THF$ (0.664 g, 1.77 mmol) was stirred in THF to give a purple solution with suspended solid. To this suspension was added 0.250 g (1.76 mmol) of LiCp* in THF, resulting in a color change from a purple to a blue-green solution. After the solution was allowed to stir for approximately 1 h, 0.93 mL of 1.9 M (1.77 mmol) CH_3Li was added resulting in a color change to dark purple. The solvent was then evaporated, and the solid was extracted with toluene. Upon addition of pentane and cooling to −30 °C, dark purple crystals of 1 (0.327 g, 0.69 mmol) were isolated in 78% yield. ^1H NMR (C_6D_6): δ −9.3 (br, Cp*, fwhm = 220 Hz). No indication of the methyl group. IR (KBr, cm^{-1}): 2978 (s), 2915 (s), 2870 (s), 1493 (s), 1427 (s), 1380 (s), 1160 (w), 1106 (s), 1085 (m), 1071 (sh), 1021 (s), 919 (w), 619 (w), 496 (s). Electrochemistry (vs Cp_2Fe/Cp_2Fe^+ in THF): irreversible oxidation −0.01 V, irreversible reductions −2.8 and −3.5 V. Anal. Calcd for $C_{11}H_{20}CrCl$: C, 55.57; H, 7.65; Cl, 14.91. Found: C, 55.39; H, 7.61; Cl, 15.04. Magnetic measurements (diamagnetic correction = -393×10^{-6} emu/g-atom): antiferromagnetically coupled, $J = -45.2$ cm^{-1}, $j = 9.3$ cm^{-1}, $P = 1.8 \times 10^{-3}$), μ_{eff}(280 K) = 3.5 μ_B.

Synthesis of Bis(μ-chloro)diethylbis(η^5-pentamethylcyclopentadienyl)dichromium(III) {(Cp*CrEtCl)$_2$} (2). Similar to synthesis of 1 (method A), 1.41 g of LiCp* (9.9 mmol) was added to 3.51 g of $EtCrCl_2 \cdot 3THF$ (9.5 mmol)[7a] in THF. Recrystallization from toluene/pentane gave 2 in 75% yield. ^1H NMR (C_6D_6): δ −9.0 (br, Cp*, fwhm = 340 Hz); no indication of the ethyl group. IR (KBr, cm^{-1}): 2973 (m), 2946 (s), 2909 (s), 2798 (m), 1499 (m), 1452 (s), 1421 (m), 1376 (s), 1357 (s), 1122 (s), 1068 (w), 1023 (s), 921 (w), 802 (w), 595 (s), 472 (s), 420 (w). Anal. Calcd for $C_{12}H_{20}CrCl$: C, 57.24; H, 8.02; Cl, 14.08. Found: C, 56.82; H, 8.04; Cl, 13.82. Magnetic measurements (diamagnetic correction = -348×10^{-6} emu/g-atom): μ_{eff}(298 K) = 3.9 μ_B.

Syntheses of Bis(μ-chloro)diphenylbis(η^5-pentamethylcyclopentadienyl)dichromium(III) {(Cp*Cr(C_6H_5)Cl)$_2$} (3). Method A. Reaction of $PhCrCl_2 \cdot 3THF$[7b] (1.00 g, 2.4 mmol) in 100 mL of THF with LiCp* (0.36 g, 2.5 mmol) resulted in an immediate color change from green to blue-purple. This solution was allowed to stir for 2 h after which it was evaporated to dryness. Extraction with toluene gave a blue-purple solution and a white solid (presumably LiCl, 0.1 g). Addition of pentane to this solution and cooling to −30 °C resulted in the isolation of 3 as dark purple crystals in 75% yield. **Method B.** $CrCl_3 \cdot 3THF$ (1.31 g, 3.48 mmol) was stirred in THF to give a purple solution with suspended solid. To this solution was added 0.05 g (3.5 mmol) of LiCp* in THF resulting in a color change from a purple to a blue-green solution. After the solution was allowed to stir for approximately 1 h, 1.45 mL of 2.4 M (3.5 mmol) PhLi was added resulting in a gradual (20–30 min) color change to a blue-purple solution. The solvent was then removed by evaporation, and the solid was extracted with toluene. With the addition of pentane and cooling dark purple crystals of 3 were isolated in 74% yield; mp 150–152 °C dec. ^1H NMR (C_6D_6): δ 13.1 (br 2 H, fwhm = 160 Hz), −11.4 (br, 15 H, fwhm = 260 Hz), −33.2 (br, 1 H, fwhm = 580 Hz), −65.8 (v br, 2 H). IR (KBr, cm^{-1}): 3010 (s), 2940 (s), 2875 (s), 1930 (w), 1850 (w), 1800 (w), 1560 (m), 1475 (w), 1370 (w), 1066 (m), 1054 (m), 1030 (s), 992 (m), 728 (s), 705 (s), 490 (m), 470 (s). MS (CI): 598 (M$^+$, 5.3%), 599 ([M + 1]$^+$, 12.6%), 521 ([M + 1 − Ph]$^+$, 100%). Anal. Calcd for $C_{16}H_{20}CrCl$: C, 64.09; H, 6.74; Cl, 11.82. Found: C, 63.93; H, 6.88; Cl, 11.76. Magnetic measurements (diamagnetic correction = -405.5×10^{-6} emu/g-atom): μ_{eff}(296 K) = 4.2 μ_B.

Synthesis of Bis(μ-chloro)dibenzylbis(η^5-pentamethylcyclopentadienyl)dichromium(III) {(Cp*Cr($CH_2C_6H_5$)Cl)$_2$} (4). To a solution of 0.26 g (0.50 mmol) of 5 in THF was added, by syringe, 0.20 mL of 2.5 M (0.50 mmol) $C_6H_5CH_2MgCl$. Over the next 15 min the solution changed from green to purple in color. The solvent was then removed by evaporation, and the solid was extracted with pentane. Upon cooling this solution, dark purple crystals of 4 (0.10 g) formed and were isolated in 66% yield. ^1H NMR (C_6D_6): δ 22.0 (br, 3 H, fwhm = 85 Hz), 1.82 (br, 2 H, fwhm = 115 Hz), −21.4 (br, 15 H, fwhm = 430 Hz). IR (KBr, cm^{-1}): 3054 (m), 3013 (m), 2977 (m), 2951 (m), 2908 (s), 1923 (w), 1844 (w), 1793 (w), 1593 (s), 1484 (s), 1446 (s), 1430 (m), 1376 (s), 1205 (s), 1069 (w), 1029 (s), 988 (m), 799 (m), 745 (s), 697 (s), 607 (m), 444 (s). Anal. Calcd for $C_{17}H_{22}CrCl$: C, 65.07; H, 7.07; Cl, 11.30. Found: C, 65.05; H, 6.93; Cl, 11.30. Magnetic measurements (diamagnetic correction = -433×10^{-6} emu/g-atom): antiferromagnetically coupled, $J = -45$ cm^{-1}, $j = 0.69$ cm^{-1}, $P = 7.3 \times 10^{-3}$, $\chi_0 = 2.4 \times 10^{-3}$ emu/mol, μ_{eff}(298 K) = 4.6 μ_B.

Synthesis of Bis(μ-chloro)dichlorobis(η^5-pentamethylcyclopentadienyl)dichromium(III) {(Cp*CrCl$_2$)$_2$} (5). To a solution of 1 (0.175 g, 0.368 mmol) in THF was added 1.1 mmol of HCl by condensation from a bulb of measured volume. As the solution warmed to room temperature, there was a color change from purple to blue-green. This solution was allowed to stir at room temperature for approximately 1 h at which time the solvent was removed by evaporation. The blue-green solid was dissolved in toluene and isolated as dark blue-green crystals by the addition of pentane and cooling to −30 °C; yield 83%. ^1H NMR (C_6D_6): δ −47.5 (br, fwhm = 480 Hz). IR (KBr, cm^{-1}): 2985 (m), 2961 (m), 2912 (m), 2854 (sh), 1490 (s), 1448 (m), 1430 (s), 1376 (s), 1073 (m), 1025 (s), 805 (w), 439 (s). MS (CI): 515 ([M + 1]$^+$, 7.6%), 517 ([M + 3]$^+$, 10.1%), 518 ([M + 5]$^+$, 5.3%). Anal. Calcd for $C_{10}H_{15}CrCl_2$: C, 46.52; H, 5.87; Cl, 27.46. Found: C, 46.71; H, 5.94; Cl, 27.39. Magnetic measurements (diamagnetic correction = 341×10^{-6} emu/g-atom): antiferromagnetically coupled, $J = -24$ cm^{-1}, $j = 3.6$ cm^{-1}, $\chi_0 = 5.6 \times 10^{-4}$ emu/mol, μ_{eff}(298 K) = 4.7 μ_B.

Synthesis of Chloromethyl(η^5-pentamethylcyclopentadienyl)(pyridine)chromium(III) {(Cp*CrCH$_3$(Cl)py)} (6). Approximately 3 mL of pyridine (py) was added to a THF solution of 1 (1.0 g, 2.1 mmol) and the mixture allowed to stir for 1 h at room temperature. Solvent was removed by evaporation, and the dark purple residue was extracted with toluene. Addition of pentane and cooling resulted in the crystallization of **6** (0.86 g) in 65% yield. ^{1}H NMR (C_6D_6): δ 20.7 (br, 2 H), −4.75 (br, 15 H), −38.3 (v br, 1 H), −45.3 (v br, 1 H). ^{1}H NMR ($CDCl_3$): δ 21.2 (br, 2.3 H), −7.2 (br, 15 H), −29.2 (br, 1 H), −42.8 (br, 1 H). IR (KBr, cm^{-1}): 3061 (w), 2913 (s), 2870 (s), 2793 (w), 1600 (s), 1480 (m), 1442 (s), 1383 (m), 1377 (m), 1213 (m), 1059 (m), 1029 (w), 1012 (w), 762 (s), 700 (s), 640 (w), 492 (s). Anal. Calcd for $C_{16}H_{23}NCrCl$: C, 60.64; H, 7.33; N, 4.42; Cl, 11.19. Found: C, 60.84; H, 7.28; N, 4.48; Cl, 11.34.

Synthesis of Chloroethyl(η^5-pentamethylcyclopentadienyl)(pyridine)chromium(III) {(Cp*CrC_2H_5(Cl)py)} (7). The synthetic procedure followed was similar to that for the synthesis of **6**. Approximately 2 mL of pyridine was added to 1.02 g (2.03 mmol) in **2** in THF. Crystallization from toluene/pentane afforded **7** (0.97 g) in 72% yield. ^{1}H NMR (C_6D_6): δ 21.7 (br, 3 H), −5.45 (br, 15 H), −26.7 (br, 3 H). Anal. Calcd for $C_{17}H_{25}NClCr$: C, 61.70; H, 7.71; N, 4.24; Cl, 10.68. Found: C, 61.76; H, 7.56; N, 4.24; Cl, 10.72.

Reaction of 1 with Excess CH_3CN. Synthesis of Chloro(4-amino-3-pentenyl-2-iminato)(η^5-pentamethylcyclopentadienyl)chromium (8). In a typical reaction 0.21 g of **1** was dissolved in 20 mL of toluene. To this solution was added about 5 mL of CH_3CN, all at once. This mixture was allowed to stir for 1 day at room temperature over which time the color of the solution changed from purple to brown. Extraction with pentane removed a black uncharacterized material and left a red-brown solid. This solid was dissolved in a minimal amount of toluene. Addition of pentane and cooling to −30 °C resulted in the isolation of a brick red microcrystalline solid (**8**) in 39% yield; mp 210 °C. ^{1}H NMR (C_6D_6): δ 53.4 (br, 6 H, fwhm = 460 Hz), 3.6 (br, 1 H), −16.1 (br, 15 H, fwhm = 420 Hz) ppm. IR (KBr, cm^{-1}): 3261 (s), 3037 (w), 2937 (s), 2912 (s), 2870 (s), 2787 (s), 1573 (s), 1537 (s), 1432 (s), 1377 (s), 1312 (m), 1107 (s), 1070 (m), 1023 (s), 769 (m), 632 (m) 619 (m), 497 (s). MS (CI): 319 (M$^+$, 40%), 320 ([M + 1]$^+$, 12%), 321 ([M + 2]$^+$, 14%). MS (FAB): 319 (M$^+$, 31.4%), 320 ([M + 1]$^+$, 13.1%), 321 ([M + 2]$^+$, 10.8%), 322 ([M + 3]$^+$, 5.7%). Anal. Calcd for $C_{15}H_{24}N_2ClCr$: C, 56.32; H, 7.58; N, 8.76; Cl, 11.08. Found: C, 56.12; H, 7.60; N, 8.53; Cl, 10.96. Magnetic measurements (diamagnetic correction: -213×10^{-6} emu/g-atom): $\mu_{eff} = 4.0\ \mu_B$, $C = 1.68$ emu/(mol·K), $\Theta = 3.56$ K, $\chi_0 = 9.42 \times 10^{-4}$ emu/mol. Electrochemistry (vs Cp_2Fe/Cp_2Fe^+ in THF): irreversible oxidation −0.2 V, irreversible reduction −2.6 and −3.2V.

Reaction of 1 with 4-Amino-2-imino-3-pentene. Independent Synthesis of 8. In a drybox 0.8 mmol of 4-amino-2-imino-3-pentene was added to a solution of **1** (0.210 g, 0.44 mmol) in 20 mL of toluene. This solution gradually turned reddish in color over the next 10 h. Filtration and evaporation of the toluene gave a brick red solid contaminated with a small amount of **1**. This solid was recrystallized from Et_2O to give a red compound spectroscopically (^{1}H NMR and IR) identical with **8** in 36% yield.

Reaction of 1 with Excess CD_3CN. Following the synthetic procedure described above for the synthesis of **8**, **1** was reacted with an excess of CD_3CN. Crystallization from a cooled toluene/pentane solution yielded a brick red solid. ^{1}H NMR (C_6D_6): δ 53.4 (br, 1.7 H), 3.6 (br s, 0.6 H), −16.1 (br, 15 H) ppm. IR (KBr, cm^{-1}): 3267 (w), 2908 (s), 2420 (s), 1552 (s), 1484 (s), 1401 (s), 1364 (m), 1069 (m), 1027 (m), 952 (w), 899 (w), 803 (w), 730 (w), 548 (s), 460 (s). Absorbance IR spectrum: ratio of absorbance of 3261 cm^{-1} (ν_{NH}):2492 cm^{-1} (ν_{ND}) = 0.084:1.0. MS (CI) (envelope of the molecular ion with substitution of the β-diketimine in the range D_xH_y, $x = 6$–9, $y = 3$–0): 325 (41.4%), 326 (20.7%), 327 (34.6%), 328 (20.8%), 329 (11.6%), 330 (6.44%).

Analysis of the CI Mass Spectrum from the Reaction of 1 and Excess CD_3CN. The mass spectrum was assumed to be made up of contributions of **8**-d_{6-9}. Percentages of each of these components were calculated by assuming a $^{35}Cl/^{37}Cl$ ratio of 75.5/24.5, a contribution to [M + 1]$^+$ of 16.5% and to [M + 2]$^+$ of 1.3% due to ^{13}C, and a ^{52}Cr:^{53}Cr:^{54}Cr ratio of 83.8:9.5:2.4.[22] By assuming that the lowest M$^+$ peak (325) was due to the d_6 species, the contributions to [M + 1]$^+$ and [M + 2]$^+$ could be calculated and subtracted from the experimental spectrum. This process was continued for the d_{7-9} species resulting in a normalized ratio of 52:11:21:16 for the d_6–d_9 components.

Reaction of 8 with Excess CD_3CN and Ethyl Dimer 2. In a glovebox 23 mg of **8** and 60 mg of **2** were combined in a round-bottom flask. The flask was equipped with a needle valve and attached to a vacuum line along with an ampule of CD_3CN. Approximately 5 mL of CD_3CN was condensed into the flask, and the mixture was allowed to stir for 2 days at which time the CD_3CN was removed under vacuum and the mixture was recrystallized from Et_2O. The resulting solid was submitted for FABMS by using sulfolane as the matrix. The mass spectrum indicated that **8** had incorporated deuterium. MS (FAB): 319 (27.1%), 320 (32.2%), 321 (22.4%), 322 (10.3%), 323 (3.0%) (compare with protio-**8** above). By using the ratios of M$^+$ to [M + 1]$^+$ (0.42) along with the ratios of M$^+$ to the higher mass peaks due to the ^{37}Cl isotope, [M + 2]$^+$ and [M + 3]$^+$ (0.34 and 0.18, respectively), which were obtained from the mass spectrum of **8**, the spectrum can be analyzed to yield a normalized ratio of d_0:d_1:d_2 of approximately 6:5:1.

Reaction of 2 with Excess C_2H_5CN (9). A solution of **2** (0.157 g, 0.312 mmol) in toluene was allowed to react with 0.46 g of propionitrile for 12 h. Following a procedure similar to that for isolation of **8**, **9** was isolated in a yield of 31%; mp 212–215 °C. ^{1}H NMR (C_6D_6): δ 41.6 (br, 2 H), 13.1 (br, 2 H, fwhm = 300 Hz), 6.2 (s, 6 H), −12.2 (br s, 15 H, fwhm = 480 Hz). Anal. Calcd for $C_{18}H_{30}ClN_2Cr$: C, 59.27; H, 8.37; N, 7.74. Found: C, 59.68; H, 8.43; N, 7.64. MS (CI): 361 (M$^+$, 64%), 362 ([M + 1]$^+$, 22%), 363 ([M + 2]$^+$, 24%). Magnetic measurements (diamagnetic correction = -248×10^{-6} emu/g-atom): μ_{eff}(299 K) = 4.0 μ_B.

Reaction of 1 with Excess C_2H_5CN (10a,b). In a reaction procedure similar to that for the synthesis of **8**, 0.217 g (0.46 mmol) of **1**, in toluene, was allowed to stir with an excess of propionitrile for 19 h. Crystallization from Et_2O gave **10** (0.120 g) in 38% yield; mp 205–213 °C melt/dec. ^{1}H NMR (C_6D_6): δ 55.2, 52.2, 41, 23.3, 10.1, 5.8, −12.4 (br, Cp*), −16.4 (br, Cp*) (consistent with two isomers, ratio of the peaks at −12.4:−16.4 of 3:2). IR (KBr, cm^{-1}): 3259 (s), 2967 (s), 2906 (s), 1567 (s), 1499 (m), 1417 (s), 1372 (s), 1314 (s), 1276 (s), 1271 (w), 1074 (m), 1000 (m), 759 (m), 482 (m), 408 (m). Anal. Calcd for $C_{17}H_{28}N_2ClCr$: C, 58.68; H, 8.13; N, 8.05; Cl, 10.19. Found: C, 58.56; H, 8.12; N, 7.95; Cl, 10.24.

Reaction of 1 with 2CH_3CN. Synthesis of (μ-Chloro)(μ-1-methylethaniminato)bis{(η^5-pentamethylcyclopentadienyl)chlorochromium(III)} (11). In a manner similar to that described below for the synthesis of **13**, **1** was reacted with 2 equiv of CH_3CN to generate a blue solid that was subsequently reacted with HCl to give **11** in an overall yield of 44%; mp 200 °C dec. ^{1}H NMR (C_6D_6): δ −40.3 (br, Cp*, fwhm = 590 Hz). IR (KBr, cm^{-1}): 2984 (m), 2910 (s), 1614 (s), 1500 (m), 1480 (s), 1447 (s), 1428 (s), 1377 (s), 1366 (s), 1217 (w), 1068 (w), 1023 (s), 804 (w), 644 (s), 501 (w), 414 (s). Anal. Calcd for $C_{23}H_{36}NCr_2Cl_3$: C, 51.44; H, 6.77; N, 2.61; Cl, 19.81. Found: C, 51.34; H, 6.88; N, 2.47; Cl, 19.44. MS (FAB): 535 (M$^+$, 12%), 537 ([M + 2]$^+$, 12%). Magnetic measurements (diamagnetic correction = -360×10^{-6} emu/g-atom): μ_{eff}(293 K) = 4.0 μ_B.

Reaction of 1 with 2C_2H_5CN. Synthesis of (μ-Chloro)(μ-1-methylpropaniminato)bis{(η^5-pentamethylcyclopentadienyl)chlorochromium(III)} (12). In a manner similar to that described below for the synthesis of **13**, **1** was reacted with C_2H_5CN to generate a blue solid that was subsequently reacted with HCl to give **12** in an overall yield of 56%; mp 205 °C dec. ^{1}H NMR (C_6D_6): δ 3.97 (br, 1 H, fwhm = 210 Hz), −41.3 (br, 6 H, fwhm = 980 Hz). IR (KBr, cm^{-1}): 2978 (m), 2911 (s), 2874 (sh), 1612 (s), 1499 (m), 1480 (m), 1460 (s), 1431 (s), 1378 (s), 1361 (m), 1209 (w), 1069 (w), 1025 (m), 965 (w), 949 (w), 804 (w), 642 (s), 617 (w), 495 (w), 461 (w), 414 (s). Anal. Calcd for $C_{24}H_{38}Cr_2Cl_3N$: C, 52.31; H, 6.97; N, 2.54; Cl, 19.30. Found: C, 52.27; H, 7.02; N, 2.45; Cl, 19.11. MS (CI): 549 (M$^+$, 5%), 550 ([M + 1]$^+$, 12%). Magnetic measurements (diamagnetic correction = -372×10^{-6} emu/g-atom): μ_{eff}(299 K) = 4.6 μ_B.

Reaction of 1 with 2C_6H_5CN. Synthesis of (μ-Chloro)(μ-1-phenylethaniminato)bis{(η^5-pentamethylcyclopentadienyl)chlorochromium(III)} (13). Compound **1** (0.42 g, 0.88 mmol) was dissolved in 20 mL of toluene. To this solution was added 0.188 g of C_6H_5CN (1.8 mmol) all at once. This mixture was stirred at room temperature for 4 h. During this time the

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(22) (a) McLafferty, F. W., Ed. *Interpretation of Mass Spectra*; University Science Books: Mill Valley, CA, 1980. (b) *CRC Handbook of Chemistry and Physics*, 59th ed.; Weast, R. C., Ed.; CRC Press Inc.: Boca Raton, FL, 1978.

Organometallics 1989, *8*, 2577–2584

solution changed color from purple to dark blue. The solvent was then removed by evaporation, and the resulting solid was extracted with toluene. Cooling resulted in the isolation of a blue solid. This solid was reacted with HCl in order to protonate the remaining methyl groups (see Scheme IV) and generate methane and an analytically pure sample. This blue solid was reacted with 1.1 equiv of HCl in THF and allowed to stir for 1–2 h. Toepler pump and GC measurements were consistent with the generation of a nonstoichiometric amount of methane (0.2 equiv). Evaporation of solvent and recrystallization from diethyl ether gave **13** with an overall yield of 43%. ^{1}H NMR (C_6D_6): δ 14.08 (br, 2.6 H, fwhm = 100 Hz), −12.68 (br, 2 H, fwhm = 120 Hz), −36.4 (br, 15 H, fwhm = 520 Hz), −41.4 (br, 15 H, fwhm = 700 Hz). IR (KBr, cm^{-1}): 3070 (w), 2982 (m), 2942 (s), 2855 (sh), 1585 (s), 1566 (s), 1492 (m), 1442 (s), 1431 (s), 1378 (s), 1361 (m), 1246 (m), 1116 (w), 1071 (w), 1026 (s), 767 (m), 747 (w), 700 (s), 646 (s), 589 (w), 481 (m), 411 (s). Anal. Calcd for $C_{28}H_{38}Cr_2NCl_3$: C, 56.17; H, 6.41; N, 2.34; Cl, 17.77. Found: C, 56.59; H, 6.61; N, 2.24; Cl, 17.39. MS (CI): 599 (M$^+$, 9%). Magnetic measurements (diamagnetic correction = -398×10^{-6} emu/g-atom): antiferromagnetically coupled, $J = -44$ cm^{-1}. $j = 4.0$ cm^{-1}, $P = 2.5 \times 10^{-3}$, $\chi_0 = 1.3 \times 10^{-3}$ cmu/mol, μ_{eff}(300 K) = 4.1 μ_B.

Reaction of 1 with Excess 2-Butyne (C_4H_6). Synthesis of Poly-2-butyne and (η^5-Pentamethylcyclopentadienyl)(η^6-hexamethylbenzene)chromium(I) {Cp*Cr(η^6-C(CH_3)$_6$)} (14). A solution of **1** (0.25 g, 0.53 mmol) in about 25 mL of toluene was charged on the vacuum line with approximately 20 mmol of 2-butyne. The reaction flask was then placed in a 60 °C oil bath for 3 days. At the end of this time the solution had changed color from a dark purple to green with a colorless insoluble solid. Filtration and washing of the solid with THF afforded 0.06 g of poly-2-butyne identified by its characteristic IR (2969 (s), 2923 (s), 2849 (s), 2711 (m), 1438 (s), 1366 (s), 1092 (s), 1028 (s), 698 (w), 526 (br, w)) and ^{1}H NMR ($CDCl_3$, 1.8 ppm) resonances;[16] mp >355 °C. Anal. Calcd for $(C_4H_6)_x$: C, 88.80; H, 11.20. Found: C, 85.49; H, 10.88. Evaporation of the solution and extraction of the solid residue with pentane gave a brown solution of **14** and a green solid (0.088 g recrystallized, 32% yield) which was identified as **5** by its IR and ^{1}H NMR signals. Cooling the pentane solution to −30 °C resulted in the isolation of **14** (0.111 g, 30% yield); mp >310 °C. ^{1}H NMR (C_6D_6): δ −12.6 (br, fwhm = 1080 Hz). IR (KBr, cm^{-1}): 2900 (s), 2943 (s), 2715 (m), 1440 (m), 1378 (s), 1283 (w), 1066 (m), 1024 (s), 493 (m), 440 (m). MS (CI): 349 (M$^+$, 19%), 350 ([M + 1]$^+$, 100%). Electrochemistry (vs Cp_2Fe/Cp_2Fe^+ in THF): reversible oxidation −1.3 V, irreversible oxidation −0.3 V, reversible reduction −3.0 V (see Figure 3). Anal. Calcd for $C_{22}H_{33}Cr$: C, 75.59; H, 9.54. Found: C, 75.97; H, 9.42. Magnetic measurements (diamagnetic correction = -257×10^{-6} emu/g-atom): μ_{eff}(296 K) = 1.9 μ_B.

Thermal Decomposition of 14. A sample of **14** (10 mg) in C_6D_6 was heated to 200 °C in a polyethylene glycol bath, and the decomposition of **14** was monitored by ^{1}H NMR. Over the next 7 days the solution took on a green color, and resonances for free hexamethylbenzene (δ 2.12) and Cp*$_2$Cr (δ −6.37) appeared and continued to grow in intensity. At the end of this time the integrated ratios of hexamethylbenzene, Cp*$_2$Cr, and **14** were 11:1:23.

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-8451670 and CHE-8512710), the donors of the Petroleum Research Fund, administered by the American Chemical Society, Amoco Foundation, E. I. du Pont de Nemours & Company, Inc., Xerox Corp., Dow Chemical Co., Rohm and Haas Co., Smith Kline and French Laboratories, and Cornell University.

Supplementary Material Available: Tables of X-ray structure determination of **13** including fractional coordinates and thermal parameters, anisotropic thermal parameters, crystal data, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

Thermodynamics of Solvation of Lithium Compounds. A Combined MNDO and ab Initio Study

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Received April 28, 1989

The solvation of the lithium cation and of (monomeric) methyllithium has been studied by semiempirical MNDO calculations for a large range of different nitrogen and oxygen bases. In addition, ab initio calculations have been performed for the solvation of methyllithium with ammonia and water. Enthalpies, entropies, and free enthalpies of solvation at different temperatures have been obtained by statistical thermodynamics at the MNDO level. General trends are discussed. The performance of MNDO has been checked against experimental values and high-level ab initio calculations. Where such comparisons are available, MNDO provides reasonable thermodynamic data. Semiempirical calculations of this type are suggested for use in the design of "optimum" solvents.

Introduction

Quantum chemical calculations[1] are a rapidly growing source of fundamental quantitative data in chemistry. They have been used, e.g., to predict structures and energies[2,3] or to gain insights into reaction pathways[4] that are otherwise hard to obtain. Because of the tremendous developments in computing power, it is possible to obtain

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