Inorganic Chemistry
Article

Synthesis, Characterization, and Electronic Structure of Diimine Complexes of Chromium

Kevin A. Kreisel,[†] Glenn P. A. Yap, and Klaus H. Theopold*

Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19716
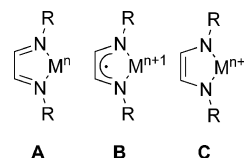
We have prepared and structurally characterized several complexes of chromium coordinated by diimine (or 1,4-diazadiene) ligands, that is, Ar—N=C(R)—(R)C=N—Ar ($^{R}L^{Ar}$) (where Ar = 2,6-diisopropylphenyl ("iPr") or 2,6-dimethylphenyl ("Me") and R = H or Me). The reaction of $CrCl_2$ with $^{H}L^{iPr}$ gave dinuclear $[(^{H}L^{iPr})Cr]_2(\mu\text{-Cl})_3(Cl)(THF)$ when isolated from Et_2O; in THF solution, however, the product exists as mononuclear $(^{H}L^{iPr})CrCl_2(THF)_2$. Two isostructural derivatives, $(^{Me}L^{Me})CrCl_2(THF)_2$ and $(^{H}L^{Me})CrCl_2(THF)_2$, have also been prepared. Furthermore, the bis-ligand complex, $(^{H}L^{iPr})_2Cr$, has been prepared along with its reduction product, $Li(THF)_4[(^{H}L^{iPr})_2Cr]$. We have also synthesized the tetracarbonyl complex, $(^{H}L^{iPr})Cr(CO)_4$, by addition of $^{H}L^{iPr}$ to $Cr(CO)_4(NCCH_3)_2$. The structure and variable temperature magnetic susceptibility of the previously reported Cr halide dimer, $[(^{H}L^{iPr})Cr(\mu\text{-Cl})]_2$, is also discussed in detail. All of the diimine complexes have been characterized structurally, spectroscopically, and magnetically, and their electronic structures are discussed with the aid of density-functional theory calculations.

Introduction

As part of our investigation of chromium alkyls as homogeneous models for commercially used heterogeneous chromium catalysts for the polymerization of ethylene and α-olefins,[1,2] we required a class of neutral, bidentate nitrogen ligands to compare the reactivity of their chromium complexes with that of the structurally related "nacnac" (i.e., α-diketiminate) derivatives. Inspired by the extensive use of diimine complexes of late transition metals in polymer-

ization catalysis,[3] we chose to initiate a study of diimines (or 1,4-diazadienes) as ancillary ligands in organochromium chemistry.

Diimine ligands are popular because of the ease of varying the steric and electronic effects that they exert upon the metal in their complexes.[4] Furthermore, the redox properties of these ligands provide an interesting electronic relationship between the ligand and the metal (see Chart 1). Diimine complexes can be classified as having electronic structures **A**, **B**, or **C** in Chart 1.[5] In the case of **A**, the diimine ligand is neutral and structurally essentially unperturbed; that is, it

Chart 1. Possible Electronic Structures of Diimine Complexes

* To whom correspondence should be addressed. E-mail: theopold@udel.edu.
† Current address: University of Wisconsin-Madison, Department of Chemistry, 1101 University Ave. Madison, WI 53706.
(1) (a) Richeson, D. S.; Hsu, S. W.; Fredd, N. H.; Van Duyne, G.; Theopold, K. H. *J. Am. Chem. Soc.* **1986**, *108*, 8273. (b) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (c) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (d) Thomas, B. J.; Mitchell, J. F.; Leary, J. A.; Theopold, K. H. *J. Organomet. Chem.* **1988**, *348*, 333. (e) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473. (f) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284.
(2) (a) Kim, W.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541. (b) MacAdams, L. A.; Kim, W.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952. (c) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2005**, *127*, 1082.

(3) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev* **2000**, *100*, 1169; and references therein.
(4) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.
(5) (a) Milione, S.; Cavallo, C.; Tedesco, C.; Grassi, A. *J. Chem. Soc., Dalton Trans.* **2002**, 1839. (b) Hannant, M. D.; Schormann, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2002**, 4071. (c) Gibson, V. C.; Tomov, A.; Wass, D. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 2261. (d) Schleis, T.; Spaniol, T. P.; Okuda, J.; Heinemann, J.; Mulhaupt, R. *J. Organomet. Chem.* **1998**, *569*, 159.

shows C−N bond distances that are in accord with double bonds and a central C−C single bond distance. Transfer of one electron from the metal to the ligand gives **B**, which can best be described as featuring a delocalized ligand-centered radical, typically with very strong antiferromagnetic coupling between any unpaired electrons on the metal and the ligand centered spin.[6] Structurally, **B** would show lengthened C−N bond distances and a shortened C−C distance compared to **A**.[7] Transfer of a second electron from the metal to the diimine ligand results in the electronic structure of **C**, that is, a coordinated enediamide.[8] **C** would show longer C−N distances yet and a short C−C distance that approaches typical double bond length. However, bond distances alone are too blunt a tool to accurately assess the degree of reduction of the ligand(s) and hence the formal oxidation state of the metal.[9] Furthermore, the truth may lie somewhere between the idealized structures of **A**, **B**, and **C**, which—after all—are but limited valence bond descriptions of particular points of a continuum.

Work on nickel diimine complexes by Wieghardt and others has greatly improved our understanding of the unique interplay between these ligands and transition metals.[10] Specifically, it has been shown that a combination of structural, spectroscopic, and computational techniques is profitably employed to fully understand the complex electronic structure of these systems, and in some cases there remains some room for argument.[11] In any event, from a reactivity viewpoint one of the attractive features of complexes of this sort is their electronic malleability; in other words, depending on the nature of the other ligands and the overall charge of the complex, the diimine ligand may relieve the metal of excess electron density or supply it when required. Functioning as a sort of "electronic buffer", coordinated diimines may thus facilitate transformations that would otherwise strain the metal's tolerance for oxidation or reduction.[12] With this idea in mind, we are exploring the reactivity of chromium coordinated by aryl-substituted diimines.
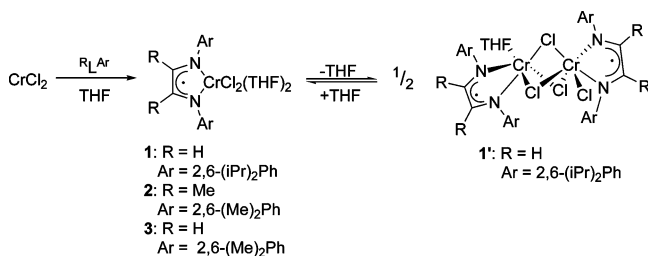
To complement our work with nacnac chromium complexes,[2] we have recently taken an interest in the organometallic chemistry of chromium supported by neutral ligands.[13] One aim of this undertaking was to synthesize cationic Cr(II) alkyl complexes to compare their reactivity with that of structurally related cationic nacnacCr(III) alkyls. Such a direct comparison might shed light on the longstanding conundrum concerning the formal oxidation state of chromium during these catalytic processes when activated by alkyl aluminum cocatalysts.[14] Diimine chromium complexes have been synthesized and studied in the past,[15] but there have been no examples of N−Aryl substituted ligands coordinated to chromium(II) except for a recent report,[16] which we believe to be in error. Herein we summarize the coordination chemistry of the diimine ligands Ar−N=C(R)−(R)C=N−Ar ($^RL^{Ar}$) (where Ar = 2,6-diisopropylphenyl ("iPr") or 2,6-dimethylphenyl ("Me") and R = H or Me) when bound to a variety of low-valent chromium fragments. Organometallic derivatives of these compounds will be the focus of a separate report.

Results and Discussion

Syntheses and Structures of ($^RL^{Ar}$)Cr Complexes. Our initial foray into chromium diimine chemistry employed the $^HL^{iPr}$ ligand and CrCl$_2$ (see Scheme 1). Thus, to a slurry of CrCl$_2$ in tetrahydrofuran (THF) was added one equivalent of $^HL^{iPr}$, to give a dark *brown* solution. After stirring overnight, solvent removal, extraction with, and crystallization from Et$_2$O produced dark *green* crystals of [($^HL^{iPr}$)Cr]$_2$-(μ-Cl)$_3$(Cl)(THF) (**1′**), which were structurally characterized by X-ray diffraction. The molecular structure of **1′** is shown in Figure 1, and selected interatomic distances and angles are listed in Table 1. The asymmetric unit of the crystal contains two independent, but chemically equivalent mol-

(6) Tsukahara, Y.; Kamatani, T.; Iino, A.; Suzuki, T.; Kaizaki, S. *Inorg. Chem.* **2002**, *41*, 4363.

(7) (a) Bart, S. C.; Hawrelak, E. J.; Schmisseur, A. K.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2004**, *23*, 237. (b) Ionkin, A. S.; Marshall, W. J. *J. Organomet. Chem.* **2004**, *689*, 1057. (c) Gardiner, M. G.; Hanson, G. R.; Henderson, M. J.; Lee, F. C.; Raston, C. L. *Inorg. Chem.* **1994**, *33*, 2456.

(8) (a) Richter, B.; Scholz, J.; Neumüller, B.; Weimann, R.; Schumann, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 365. (b) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3294.

(9) (a) Rindorf, G.; Thorup, N.; Bjornhom, T.; Bechgaard, K. *Acta. Cryst., Sect. C* **1990**, *C46*, 1437. (b) Ray, K.; Weyhermüller, T.; Goossens, A.; Crajé, M. W. J.; Wieghardt, K. *Inorg. Chem.* **2003**, *42*, 4082.

(10) (a) Balch, A.; Holm, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 5201. (b) Walther, D. *Z. Anorg. Allg. Chem.* **1974**, *405*, 8. (c) Khusniyarov, M. M.; Harms, K.; Burhaus, O.; Sundermeyer, J. *Eur. J. Inorg. Chem.* **2006**, 2985. (d) Herebain, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2003**, *125*, 9116. (e) Herebain, D.; Wieghardt, K.; Neese, F. *J. Am. Chem. Soc.* **2003**, *125*, 10997. (f) Chlopek, K.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2006**, *45*, 6298. (g) Muresan, N.; Chlopek, K.; Weyhermüller, T.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2007**, *46*, 5327. (h) Muresan, N.; Weyhermüller, T.; Wieghardt, K. *Dalton Trans.* **2007**, 4390.

(11) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.

(12) (a) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2005**, *44*, 5559. (b) Haneline, M. R.; Heyduk, A. F. *J. Am. Chem. Soc.* **2006**, *128*, 8410. (c) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2008**, *47*, 265. (d) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400.

(13) (a) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Organometallics* **2006**, *25*, 4670. (b) Kreisel, K. A.; Yap, G. P. A.; Theopold, K. H. *Chem. Commun.* **2007**, 1510.

(14) (a) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485. (b) Rahim, M.; Taylor, N. J.; Xin, S. X.; Collins, S. *Organometallics* **1998**, *17*, 1315. (c) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947. (d) McGuinness, D. S.; Brown, D. B.; Tooze, R. P.; Hess, F. M.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2006**, *25*, 3605. (e) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc.* **2006**, *128*, 9238.

(15) (a) Franz, K. D.; tom Dieck, H.; Krynitz, U.; Renk, I. W. *J. Organomet. Chem.* **1974**, *64*, 361. (b) tom Dieck, H.; Kinzel, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 324. (c) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015. (d) Bell, A.; Walton, R. A. *Polyhedron* **1986**, *5*, 951. (e) Bell, A.; Walton, R. A. *Polyhedron* **1986**, *5*, 1321. (f) Holzmeier, P.; Goerner, H.; Knoch, F.; Kisch, H. *Chem. Ber.* **1989**, *122*, 1457. (g) Grevels, F.-W.; Kayran, C.; Ozkar, S. *Organometallics* **1994**, *13*, 2937. (h) Bildstein, B.; Malaun, M.; Kopacka, H.; Fontani, M.; Zanello, P. *Inorg. Chim. Acta* **2000**, *300−302*, 16.

(16) Turki, T.; Guerfel, T.; Bouachir, F. *Inorg. Chem. Commun.* **2006**, *9*, 1023; We believe that the diamagnetism of the tetrahedral (diimine)MCl$_2$ complexes as well as the crystal structure of **2b2** reported in this paper are more consistent with zinc complexes—zinc was used as a reducing agent. We have communicated our view to the authors.

Scheme 1. Synthesis of Diimine Cr Halide Complexes **1**, **2**, **3**, and **1′**

1: R = H
Ar = 2,6-(iPr)$_2$Ph
2: R = Me
Ar = 2,6-(Me)$_2$Ph
3: R = H
Ar = 2,6-(Me)$_2$Ph

1′: R = H
Ar = 2,6-(iPr)$_2$Ph

ecules; only one of these is shown in Figure 1. In the solid state, **1′** is an unsymmetric, dinuclear complex with both chromium atoms exhibiting distorted octahedral coordination. Each chromium atom is coordinated by a diimine ligand and three bridging chlorides; the dissymmetry is introduced by a THF molecule coordinated to Cr(1), while Cr(2) is bonded to a terminal chloride ligand. The Cr−Cl distances to the bridging chlorides range from 2.350(1) to 2.452(1) Å and fall within the range of other bridging chloride complexes of chromium (2.293−2.813 Å; avg = 2.397 Å).[17] The shorter Cr−Cl distances of the terminal chlorides are also unexceptional at 2.279(1) and 2.291(1) Å. The Cr−N distances range from 1.964(4) to 1.993(4) Å and are slightly shorter than most other reported Cr(II)−N bond lengths (avg = 2.079 Å).[18]

More interesting are the C−N and C−C bond distances of the diimine ligands, which deviate substantially from those of the free ligand (C−N, 1.2632(2) Å; C−C, 1.468(2) Å).[7c] The average C−N distance in **1′** is 1.333(5) Å, whereas the average C−C distance is only marginally longer at 1.391(6) Å. These distances suggest some reduction of the diimine ligand, possibly amounting to the formation of a ligand centered radical (i.e., **B** in Chart 1).[10g,h] Consequently, the Cr atoms in **1′** may be best described as adopting the Cr(III) oxidation state. The room temperature magnetic moment of **1′** ($\mu_{\text{eff}} = 2.8(1)$ μ_B per Cr) is consistent either with quartet Cr(III) strongly antiferromagnetically coupled to a ligand centered radical ($S = \frac{1}{2}$) or, however improbable, with low spin octahedral Cr(II) (d^4, $S = 1$). The distance between the two chromium atoms (Cr(1)−Cr(2) = 3.090(4) Å) militates against metal−metal bonding, and the agreement between measured and expected magnetic moment renders significant antiferromagnetic coupling between the Cr atoms unlikely. Indeed, the effective magnetic moment of **1′** is similar to that of the monomeric species **3** (vide infra), strongly suggesting that each Cr atom in **1′** is acting as an isolated paramagnet. We suggest that the most appropriate description of the electronic structure of **1′** is as a dinuclear complex containing two noninteracting Cr(III) ions, each coordinated by, and antiferromagnetically coupled to a diimine radical anion.

Green CD$_2$Cl$_2$ solutions of **1′** showed very broad and isotropically shifted resonances in the ^{1}H NMR spectrum,

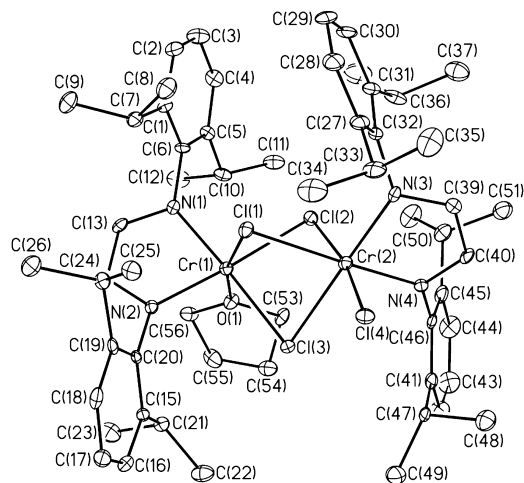(17) A search of the Cambridge Structural Database for chloride ligands bridging two chromium atoms resulted in 116 hits. Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.
(18) A search of Cambridge Structural Database for Cr(II) complexes with single Cr-N bonds resulted in 832 hits. Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.

Figure 1. ORTEP plot of one of the two independent molecules of [($^{\text{H}}$L$^{\text{iPr}}$)Cr]$_2$(μ-Cl)$_3$(Cl)(THF) (**1′**) at the 30% probability level. Hydrogen atoms have been omitted for clarity.

with overlapping peaks at 16.1, 0.51, −1.9, −7.4, and −21.2 ppm. In contrast, solutions of **1′** in THF-d_8 were *brown* and revealed a dramatically different spectrum with resolved resonances at 20.0, 0.27, −1.9, and −10.2 ppm. These ^{1}H NMR data, as well as the structures of the related complexes **2** and **3** suggest that in THF solution **1′** dissociates into mononuclear ($^{\text{H}}$L$^{\text{iPr}}$)CrCl$_2$(THF)$_2$ (**1**). Unfortunately, the high solubility of **1** in THF precluded its crystallization and structural characterization.

Reaction of $^{\text{Me}}$L$^{\text{Me}}$ or $^{\text{H}}$L$^{\text{Me}}$ with CrCl$_2$ in THF gave similar *brown* solutions (see Scheme 1). Crystallization of these products from THF afforded ($^{\text{Me}}$L$^{\text{Me}}$)CrCl$_2$(THF)$_2$ (**2**) and ($^{\text{H}}$L$^{\text{Me}}$)CrCl$_2$(THF)$_2$ (**3**). The molecular structure of **2**, as determined by X-ray diffraction, is shown in Figure 2; its interatomic distances and angles are listed in Table 2. **2** features slightly distorted octahedral coordination, with *cis* bond angles ranging from 79.68(6)° to 96.48(5)° and *trans* angles ranging from 170.87(2)° to 174.95(6)°. The terminal chloride distances in **2** (2.309(1) and 2.340(1) Å) are similar to those in **1′**, as are the Cr−N distances (1.983(2) and 1.969(2) Å). The Cr−O$_{\text{THF}}$ distances of 2.148(2) and 2.154(2) Å are also on par with other reported THF complexes of chromium.[19] Like **1′**, **2** shows evidence of diimine reduction with C−N distances of 1.347(2) and 1.343(2) Å and a C−C distance of 1.407(2) Å. Once again, this suggests the existence of a radical centered on the diimine ligand. The molecular structure and metric data of **3** are similar to those of **2** and therefore the full structural details have been relegated to the Supporting Information. **3**, and by analogy **2** (see Experimental Section), has a magnetic moment of 2.9(1) μ_B which is consistent with an $S = 1$ spin state. The same options as described above for **1′** exist, and akin to the latter, the electronic structures of **2** and **3** are most straightforwardly rationalized by invoking strong antiferro-

(19) (a) Bazan, G. C.; Rogers, J. S.; Fang, C. C. *Organometallics* **2001**, *20*, 2059. (b) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (c) Dionne, M.; Jubb, J.; Jenkins, H.; Wong, S.; Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1874.

Table 1. Selected Interatomic Distances (Å) and Angles (°) for One of the Two Independent Molecules of [(^{H}L^{iPr})Cr]$_2$(μ-Cl)$_3$(Cl)(THF) (**1'**)

Distances (Å)							
Cr(1)−Cl(1)	2.350(1)	Cr(1)−Cl(2)	2.381(1)	Cr(1)−Cl(3)	2.373(1)	Cr(1)−N(1)	1.987(4)
Cr(1)−N(2)	1.986(4)	Cr(1)−O(1)	2.065(3)	Cr(1)−Cr(2)	3.090(4)	Cr(2)−Cl(1)	2.432(1)
Cr(2)−Cl(2)	2.406(1)	Cr(2)−Cl(3)	2.452(1)	Cr(2)−Cl(4)	2.279(1)	Cr(2)−N(3)	1.964(4)
Cr(2)−N(4)	1.972(4)	N(1)−C(13)	1.328(5)	N(2)−C(14)	1.343(5)	N(3)−C(39)	1.328(5)
N(4)−C(40)	1.334(5)	C(13)−C(14)	1.386(6)	C(39)−C(40)	1.396(6)		

Angles (°)					
N(1)−Cr(1)−N(2)	81.0(2)	N(1)−Cr(1)−O(1)	94.1(1)	N(2)−Cr(1)−O(1)	95.1(1)
N(1)−Cr(1)−Cl(1)	95.9(1)	N(1)−Cr(1)−Cl(2)	96.0(1)	N(1)−Cr(1)−Cl(3)	177.4(1)
O(1)−Cr(1)−Cl(1)	165.80(9)	O(1)−Cr(1)−Cl(2)	87.19(9)	O(1)−Cr(1)−Cl(3)	86.05(9)
N(3)−Cr(2)−N(4)	81.1(2)	N(3)−Cr(2)−Cl(1)	99.5(1)	N(3)−Cr(2)−Cl(2)	95.9(1)
N(3)−Cr(2)−Cl(3)	179.4(1)	N(3)−Cr(2)−Cl(4)	91.2(1)		

magnetic coupling between a Cr(III) ion and an adjacent diimine ligand radical anion.

In an effort to access lower oxidation state complexes of chromium, we began metalating with the one electron reduced form of the diimine ligand, Na[^{H}L^{iPr}], which was formed in situ by reduction with sodium metal (see Scheme 2).[20] Addition of dark red THF solutions of Na[^{H}L^{iPr}] to a slurry of CrCl$_2$ in THF did not produce the expected [(^{H}L^{iPr})Cr(μ-Cl)]$_2$ (**4**, vide infra), but rather the red-brown bis-ligand complex (^{H}L^{iPr})$_2$Cr (**5**) in <30% yield along with unreacted CrCl$_2$. Accordingly, **5** could be readily prepared in much better yield by slow addition of two equivalents of Na[^{H}L^{iPr}] to CrCl$_2$ in THF. Interestingly, complexes **1**−**3** can be synthesized by mixing Na[^{R}L^{Ar}] and CrCl$_3$(THF)$_3$ in equimolar ratios. The solid-state structure, distances, and angles for **5** can be found in Figure 3 and Table 3. *Formally* a Cr(0) complex, **5** exhibits distorted square planar coordination (31.5° dihedral angle between the diimine ligand planes) with a crystallographically imposed inversion center situated at Cr; it is isomorphous to a previously reported nickel complex.[21] Despite the lower coordination number, the Cr−N bond distances of 2.030(4)Å and 2.035(4)Å are longer than those in complexes **1**−**3**. Once again, the diimine ligands show clear signs of reduction, with C−N distances of 1.334(10) and 1.328(11) Å and a C−C distance of 1.406(12) Å. These metric parameters suggest that **5** contains a Cr(II) ion ($S = 2$) coordinated by two diimine radical anions rather than Cr(0) with neutral diimine ligands, as was suggested previously for a *N,N'*-dicyclohexyl substituted bis-diimine complex of chromium.[15b]

Complex **5** was cleanly reduced by one electron in a reaction with LiCH$_2$SiMe$_3$ to produce what is *formally* a Cr(-I) "ate" complex, namely Li(THF)$_4$[(^{H}L^{iPr})$_2$Cr] (**6**) (see Scheme 2). Green crystals of **6** were grown from Et$_2$O at −30 °C, and the molecular structure as determined by X-ray diffraction is shown in Figure 4; structural data can be found in Table 4. Similar to **5**, complex **6** exhibits distorted square planar geometry, with the dihedral angle of the diimine ligands being nearly identical at 32.3°. Of considerable interest are the Cr−N bond distances, which range from 1.995(2) to 2.013(2) Å, that is, marginally shorter than those in **5**. However, the more remarkable difference between the structures of **5** and **6** lies in the C−N and C−C distances of

the diimine ligands. The C−N distances of **6** are significantly longer than those in **1**−**5** at 1.382(3), 1.377(3), 1.375(4), and 1.379(3) Å. At the same time, the C−C distances are shortened to 1.344(4) and 1.348(4) Å, essentially C=C double bond distances. These distances might suggest that the diimine ligands in **6** have now been reduced to the dianionic, enediamide form (**C** in Chart 1), which would then require the metal to be Cr(III). Besides the counterintuitive notion of such a "reductively induced oxidation" of the metal, the nearly identical coordination geometries of **5** and **6** also argue against a change in metal oxidation state. An alternative description of **6** would maintain chromium in the +II oxidation state, coordinated by one dianionic enediamide ligand and one monoanionic, ligand centered radical, similar to K(THF)$_4$[Zn(^{H}L^{tBu*})$_2$] (where ^{H}L^{tBu*} is ^{t}BuN=CH−CH= N^{t}Bu).[7c,10g,22] Unlike the zinc example, it is apparent from the C−N and C−C bond distances that the radical is not localized on either one of the two ligands.

Variable temperature magnetic measurements were carried out on **5** and **6** (see Supporting Information). Complex **5** displayed a slightly temperature dependent moment increasing with temperature from 2.2(1) to 2.7(1) μ_B (30−300 K); the room temperature value is close to the spin only value for two unpaired electrons ($\mu_{eff} = 2.83$ μ_B for $S = 1$). The cause of the temperature dependence is not entirely clear, but it could be due to weak intermolecular coupling between adjacent molecules. Complex **6** showed no temperature dependence with a moment of 3.9(1) μ_B (10−300 K) indicating the presence of three unpaired electrons. Neither **5** nor **6** showed any obvious signs of antiferromagnetic coupling between the metal and a ligand-centered radical, but this is to be expected as the relevant metal−ligand coupling constants have been calculated to be very large.[23] Indeed, both complexes adhered to the Curie−Weiss law with Curie constants of 0.773 emu K/mol and 1.98 emu K/mol and Weiss constants of −7.7 and −1.9 K for **5** and **6**, respectively. Unfortunately, these magnetic measurements do not differentiate between Cr(II) and Cr(III) for either **5** or **6**. We suggest that **5** exists as Cr(II) ($S = 2$) coordinated by two ligand-centered radicals ($S = $ $^1/_2$), which results in an overall spin state that matches well with the room temperature moment of 2.7(1) μ_B. The electronic structure for **6** is more difficult to discern; however, the unchanged

(20) Scholz, A.; Thiele, K.-H.; Scholz, J.; Weimann, R. *J. Organomet. Chem.* **1995**, *501*, 195.

(21) Bonrath, W.; Pörschke, K. R.; Mynott, R.; Krüger, C. *Z. Naturforsch. B* **1990**, *45B*, 1647.

(22) Rijnberg, E.; Richter, B.; Thiele, K.-H.; Boersma, J.; Lee, F. C.; Raston, C. L. *Inorg. Chem.* **1998**, *37*, 56.

(23) Kapre, R. R.; Bothe, E.; Weyhermüller, T.; DeBeer George, S.; Muresan, N.; Wieghardt, K. *Inorg. Chem.* **2007**, *46*, 7827.
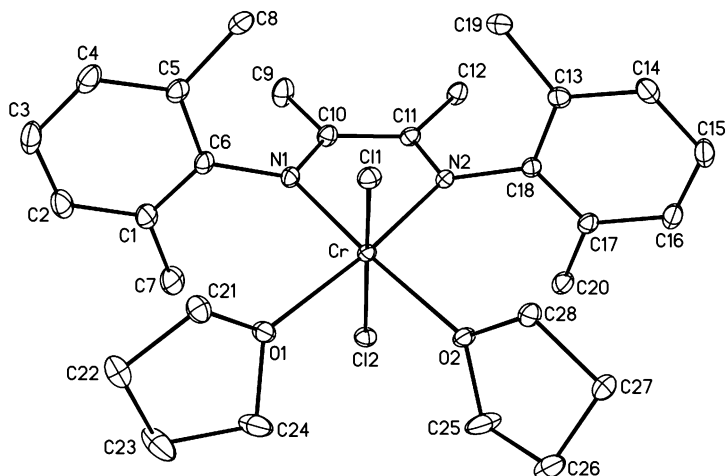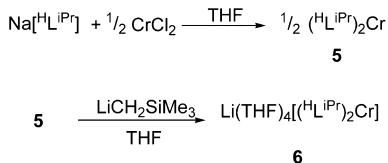
Figure 2. ORTEP plot of $(^{Me}L^{Me})CrCl_2(THF)_2$ (**2**) at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (°) for $(^{Me}L^{Me})CrCl_2(THF)_2$ (**2**)

Distances (Å)							
Cr−Cl(1)	2.310(1)	Cr−Cl(2)	2.340(1)	Cr−O(1)	2.154(2)	Cr−O(2)	2.148(2)
Cr−N(1)	1.983(2)	Cr−N(2)	1.969(2)	N(1)−C(10)	1.347(2)	N(2)−C(11)	1.343(2)
C(10)−C(11)	1.407(2)						

Angles (°)							
Cl(1)−Cr−Cl(2)	170.86(2)	O(1)−Cr−O(2)	90.98(5)	N(1)−Cr−O(2)	174.95(6)		
N(2)−Cr−O(1)	173.27(6)	N(1)−Cr−N(2)	79.68(6)	O(1)−Cr−O(2)	90.98(5)		

Scheme 2. Synthesis of Complexes **5** and **6**

$$Na[^HL^{iPr}] + {}^1/_2\ CrCl_2 \xrightarrow{\text{THF}} {}^1/_2\ (^HL^{iPr})_2Cr$$
5

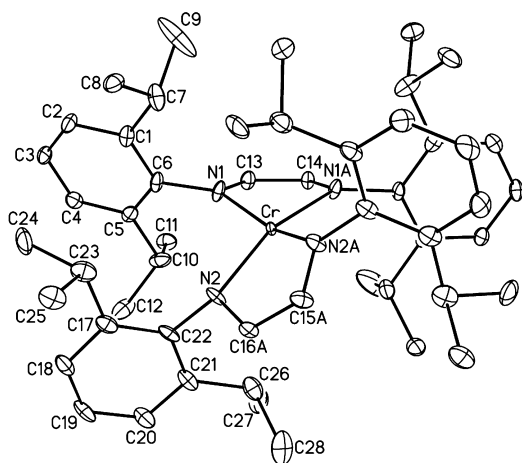$$\textbf{5} \xrightarrow[\text{THF}]{\text{LiCH}_2\text{SiMe}_3} Li(THF)_4[(^HL^{iPr})_2Cr]$$
6

dihedral angle between the diimine ligands around Cr suggests Cr(II) as well, thus requiring one diamagnetic, dianionic, enediamide ligand ($S = 0$) and one anionic, ligand-centered radical ($S = {}^1/_2$) giving an overall $S = {}^3/_2$ spin state.

The targeted chloride dimer $[(^HL^{iPr})Cr(\mu\text{-Cl})]_2$ (**4**) was ultimately prepared by reacting a THF solution of the dianion of $^HL^{iPr}$, $Na_2[^HL^{iPr}]$ (also prepared in situ), with $CrCl_3(THF)_3$ according to Scheme 3.[21] Although **4** and its magnetochem-

Figure 3. ORTEP plot of $(^HL^{iPr})_2Cr$ (**5**) at the 30% probability level. Hydrogen atoms have been omitted for clarity.

istry have been communicated previously,[24] a detailed structural and electronic analysis has not been presented and this is done here. The Cr−Cl bond lengths in **4** of 2.375(1), 2.375(1), 2.377(2), and 2.379(2) Å are similar to those for **1′**, as are the Cr−N distances of 1.984(4)Å, 1.989(4)Å, 1.989(3)Å, and 1.990(3)Å. In addition, the diimine ligands show signs of reduction to ligand-centered radicals with an average C−N distance of 1.341(6) Å and an average C−C distance of 1.388(6) Å. This assignment would then require two Cr(II) ions (d^4, $S = 2$), which would presumably couple antiferromagnetically to two ligand centered radicals giving a local net $S = {}^3/_2$ spin state per Cr and an expected spin only moment of 3.88 μ_B per Cr.

A room temperature magnetic susceptibility measurement on **4** gave a lower than expected moment of 4.8(1) μ_B (i.e., 3.4(1) μ_B per Cr). In view of the long Cr−Cr distance in **4** (3.431(1)Å), which precludes any meaningful Cr−Cr bonding, this points to weak antiferromagnetic coupling between the metals as the cause of the lowered moment. Accordingly, a variable temperature magnetic susceptibility measurement showed typical antiferromagnetic coupling between two paramagnetic centers. To correctly fit the χ_m vs T curve,[25] the spin multiplicity of the individual halves of **4** was required. Therefore, $Et_4N[(^HL^{iPr})CrCl_2]$ (**7**) was synthesized from **4** by the addition of excess NEt_4Cl in THF. Single crystals of **7** were grown from Et_2O at −30 °C, and Figure

(24) Kreisel, K. A.; Yap, G. P. A.; Dmitrenko, O.; Landis, C. R.; Theopold, K. H. *J. Am. Chem. Soc.* **2007**, *129*, 14162.
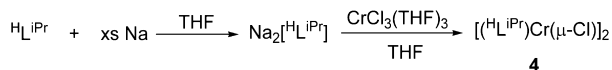
(25) (a) Griffith, J. S. *Struct. Bonding (Berlin)* **1972**, *10*, 87. (b) *The Theory of Electric and Magnetic Susceptibilities*; Van Vleck, J. H., Ed.; Oxford University Press: London, 1932. (c) *Magnetic Properties of Coordination and Organometallic Tranistion Metal Compounds, Landolt-Bornstein Series*; Hellwege, K.-H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1981; Vol. *11*.

Table 3. Selected Interatomic Distances (Å) and Angles (°) for (HLiPr)2Cr (**5**)

|							
Distances (Å)							
Cr−N(1)	2.035(4)	Cr−N(2)	2.030(4)	N(1)−C(13)	1.334(10)	N(2)−C(16A)	1.328(11)
C(13)−C(14)	1.406(12)	C(15A)−C(16A)	1.382(12)				
Angles (°)							
N(1)−Cr−N(1A)	81.8(2)	N(1)−Cr−N(2A)	159.5(2)	N(1)−Cr−N(2)	102.3(2)		
N(2)−Cr−N(2A)	81.0(2)						

Table 4. Selected Interatomic Distances (Å) and Angles (°) for Li(THF)4[(HLiPr)2Cr] (**6**)

Distances (Å)							
Cr−N(1)	2.013(2)	Cr−N(2)	2.001(2)	Cr−N(3)	1.995(2)	Cr−N(4)	2.007(2)
N(1)−C(13)	1.382(3)	N(2)−C(14)	1.377(3)	N(3)−C(39)	1.375(3)	N(4)−C(40)	1.379(3)
C(13)−C(14)	1.344(4)	C(39)−C(40)	1.348(4)				
Angles (°)							
N(1)−Cr−N(2)	81.46(9)	N(1)−Cr−N(3)	158.6(1)	N(1)−Cr−N(4)	105.81(9)		
N(2)−Cr−N(3)	99.27(9)	N(2)−Cr−N(4)	159.4(1)	N(3)−Cr−N(4)	81.02(9)		

Scheme 3. Synthesis of the Cr Halide Dimer, Complex **4**

$$HL^{iPr} + \text{xs Na} \xrightarrow{\text{THF}} Na_2[^{H}L^{iPr}] \xrightarrow[\text{THF}]{CrCl_3(THF)_3} [(^{H}L^{iPr})Cr(\mu\text{-Cl})]_2$$
4

5 and Table 5 show the results of the X-ray diffraction study. The Cr atom in **7** is set in a slightly distorted square planar geometry with coordination by two terminal chloride ligands and a diimine ligand. Similar to the previously described halide complexes **1**−**4**, the Cr−Cl bond distances in **7** are
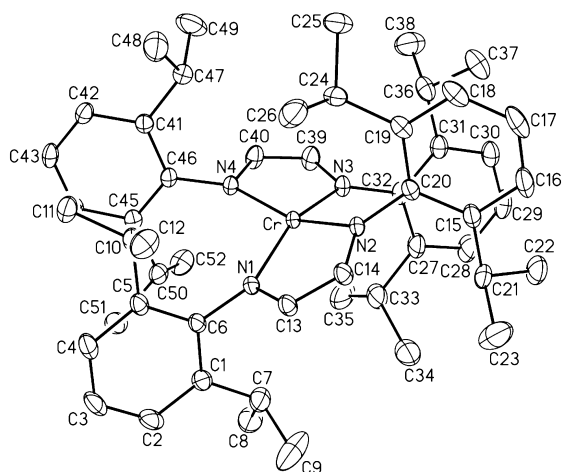
Figure 4. ORTEP plot of Li(THF)4[(HLiPr)2Cr] (**6**) at the 30% probability level. The Li(THF)4+ cation and hydrogen atoms have been omitted for clarity.
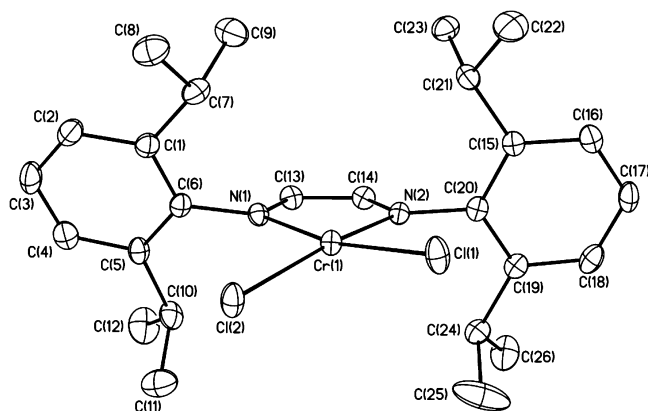
Figure 5. ORTEP plot of one of the two independent molecules of Et4N[(HLiPr)CrCl2] (**7**) at the 30% probability level. The Et4N+ cation and hydrogen atoms have been omitted for clarity.

2.330(2) and 2.345(2)Å, whereas the Cr−N distances are longer than in the previous examples at 2.013(2) and 2.020(2)Å. **7** apparently contains a reduced diimine ligand much like that of **4**, with C−N distances of 1.346(3) and 1.347(3) Å and a C−C distance of 1.374(4) Å. Using the same reasoning as before, **7** should be considered a high spin Cr(II) with an antiferromagnetically coupled ligand-centered radical, identical to the situation for each paramagnetic center in **4**. The room temperature effective magnetic moment of **7** was 3.9(1) μ_B, consistent with an $S = {}^3/_2$ system. Using this value, a fit of the variable temperature magnetic data for **4** with $S_{1, 2} = {}^3/_2$ gave a coupling constant of $J = -17 \text{ cm}^{-1}$.[24]

Like the THF-d_8 solutions of **1**−**3**, complex **4** exhibited a simple paramagnetic ^{1}H NMR spectrum in C6D6 with resonances at 17.7, 1.56, and −17.3 ppm. **4** can also bind one or two THF ligands. A crystal structure of the unsymmetric, mono-THF complex (**4·THF**) can be found in the Supporting Information. The mono-THF complex can be identified by ^{1}H NMR resonances at 17.2, 2.07, 0.45, and −18.9 ppm while the bis-THF complex featured resonances at 17.9, 6.52, 0.70, and −16.9 ppm. We believe that the latter complex should also be dimeric by comparison to the structurally similar β-diketiminate chromium complex [(($^iPr_2C_6H_3$)2nacnac)Cr(μ-Cl)(THF)]2.[26]

Electronic Structures of Complexes 1−7. Owing to the redox properties of diimine ligands, the assignment of the electronic structures of the diimine ligands, and the associated metal oxidation states in **1**−**7**, are somewhat problematic. Table 6 shows the C−N and C−C bond distances of the diimine ligands for **1**−**7**, along with the bond distances for the three oxidation levels of HLiPr.[7c,27] With the exception of complexes **6** and **8** (vide infra), all of the C−N bond distances fall within 0.021 Å of each other, and the C−C distances are within 0.032 Å of one another. Comparison of these distances with the values for the free ligand makes it apparent that the diimine ligands are reduced roughly to the extent of a one electron reduced, ligand-centered radical. Examination of the C−N and C−C bond lengths of **6** reveal that its diimine ligands have a different electronic structure than the other diimine complexes; the ligands here are even further reduced.[27]

(26) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895.
(27) Chen, R.; Tatsumi, K. *J. Coord. Chem.* **2002**, *55*, 1219.

Table 5. Selected Interatomic Distances (Å) and Angles (°) for One of the Two Independent Molecules of Et$_4$N[(^{H}L^{iPr})CrCl$_2$] (**7**)

Distances (Å)							
Cr(1)−Cl(1)	2.330(2)	Cr(1)−Cl(2)	2.345(2)	Cr(1)−N(1)	2.020(2)	Cr(1)−N(2)	2.013(2)
N(1)−C(13)	1.346(3)	N(2)−C(14)	1.347(3)	C(13)−C(14)	1.374(4)		

Angles (°)					
Cl(1)−Cr(1)−Cl(2)	94.83(4)	N(1)−Cr(1)−N(2)	79.2(1)	Cl(1)−Cr(1)−N(1)	168.71(7)
Cl(2)−Cr(1)−N(2)	168.14(7)				

Table 6. C−N and C−C Bond Distances (Å) for Complexes **1′**−**8**, ^{H}L^{iPr}, [^{H}L^{iPr}]$^{−1}$, and [^{H}L^{iPr}]$^{−2}$

compound	C−N distance	C−C distance
^{H}L^{iPr}	1.263(2)	1.468(2)
[^{H}L^{tBu*}]$^{−1a}$	1.32(1), 1.33(1)	1.41(1), 1.40(1)
[^{H}L^{iPr}]$^{−2b}$	1.423(4), 1.409(4), 1.403(4), 1.431(4)	1.352(4), 1.355(4)
1′-dimer	1.328(5), 1.343(5), 1.328(5), 1.334(5)	1.386(6), 1.396(6)
2	1.347(2), 1.343(2)	1.407(2)
3	1.326(5), 1.340(5)	1.385(6)
4	1.331(5), 1.350(6), 1.339(6), 1.342(5)	1.387(6), 1.389(6)
5	1.334(10), 1.328(11)	1.406(12)
6	1.382(3), 1.377(3), 1.375(4), 1.379(3)	1.344(4), 1.348(4)
7	1.346(3), 1.347(3)	1.374(4)
8	1.298(3), 1.297(3)	1.433(3)

^{a} From reference 7c; t-butyl groups are bound directly to the diimine nitrogen atoms. ^{b} From reference 27.

To gain a more complete understanding of the electronic structures of these molecules, density-functional theory (DFT) calculations were carried out on bis-ligand complexes **5** and **6**, as well as dichloride **7** at the B3LYP/6−311 g level using simplified model complexes in which the 2,6-diisopropylphenyl groups were replaced with methyl groups, that is, (^{H}L^{Me*})$_2$Cr (**5′**), [(^{H}L^{Me*})$_2$Cr]$^−$ (**6′**) and [(^{H}L^{Me*})CrCl$_2$]$^−$ (**7′**).[28] A spin-unrestricted calculation on **5′** resulted in metric parameters that were in good agreement (ΔCr−N < 0.02 Å, ΔC−N < 0.03 Å, ΔC−C < 0.01 Å) with the X-ray data of **5** (see Table 3). Even with the sterically less demanding ligands, the calculated dihedral angle between the diimine ligands about the Cr atom was 29.0°, very close to the experimental value of 31.5°, indicating an electronic preference for this particular geometry. A self-consistent field (SCF) population analysis showed four singly occupied metal-based orbitals in the spin-up configuration while each of the diimine ligands carried one electron in the spin-down configuration (see Figure 6). The Mulliken spin density also supported this description, with ∼3.9 electrons at Cr and ∼1.9 electrons of opposite spin distributed over the diimine ligands. With respect to the oxidation state formalism, these calculations nicely corroborate our hypothesis that **5** indeed contains Cr(II) coordinated by two ligand-centered diimine radicals.

As suggested earlier, the electronic structure of anionic **6** is more complex and at least two electronic situations are conceivable. The first couples Cr(II) with one ligand-centered radical anion and one dianionic, enediamide ligand. The second posits Cr(III) coordinated by two enediamide ligands. Both descriptions would be consistent with the experimentally confirmed quartet spin ground state. Once again, a spin-unrestricted structure optimization of **6′** gave metric parameters that were in good agreement (ΔCr−N ≤ 0.025 Å, ΔC−N < 0.025 Å, ΔC−C < 0.025 Å) with the experimen-

tally determined structure of **6** (see Table 4), including the ligand dihedral angle about the metal (calc = 28.1°, exp = 32.3°). A population analysis of **6′** showed three singly occupied, mostly metal-based orbitals and one orbital of mixed metal/ligand character. In addition, two ligand-based MOs were found to be populated: one doubly occupied, entirely ligand-based MO and one singly occupied MO that includes some metal character (see Figure 7).

Finally, a geometry optimization of **7′** produced metric parameters that were generally in excellent agreement (ΔCr−N < 0.03 Å, ΔC−N < 0.02 Å, ΔC−C < 0.02 Å) with the X-ray data (see Figure 5 and Table 5), except for the Cr−Cl distances, which were poorly reproduced with a ΔCr−Cl of nearly 0.1 Å. A population analysis of **7′** gave results that resembled those for **5′**, namely a Cr(II) ion (d^4, S = 2) coupled to a ligand-centered radical, giving an overall spin state of S = $^3/_2$ (see Figure 8).

One caveat to the electronic description of **7′** is that the metal-based orbitals are not pure; they are mixed with p-orbitals of the chloride ligands. Nevertheless, the calculated Mulliken spin density shows ∼3.9 electrons centered at Cr with ∼0.9 electrons spread over the diimine ligand and carrying the opposite spin. Thus, it would seem that **7**, and by extension **4**, are only *formally* Cr(I) complexes; an
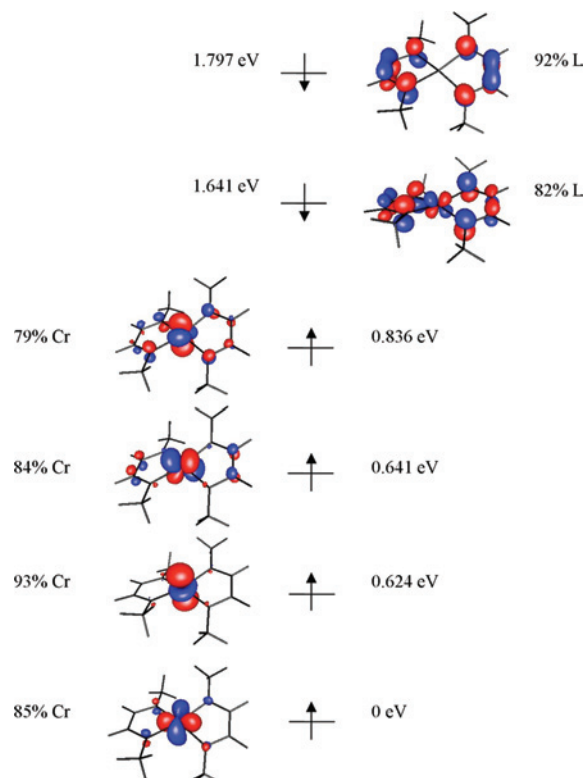
Figure 6. Qualitative MO diagram of **5′** showing the singly occupied molecular orbitals (SOMOs, labeled with percentage of major contribution) that give rise to the S = 1 spin state of **5**.

(28) The calculations were performed using Gaussian 03 software: Frisch, M. J.; et al. *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburg, PA, 2003 (see Supporting Information for complete citation).
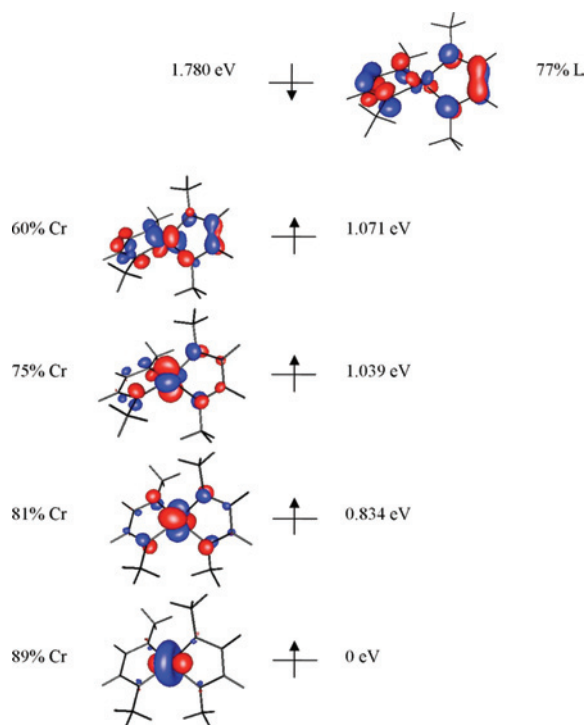
Figure 7. Qualitative MO diagram of **6′** showing the SOMOs (labeled with percentage of major contribution) that give rise to the $S = {}^3/_2$ spin state of **6**.
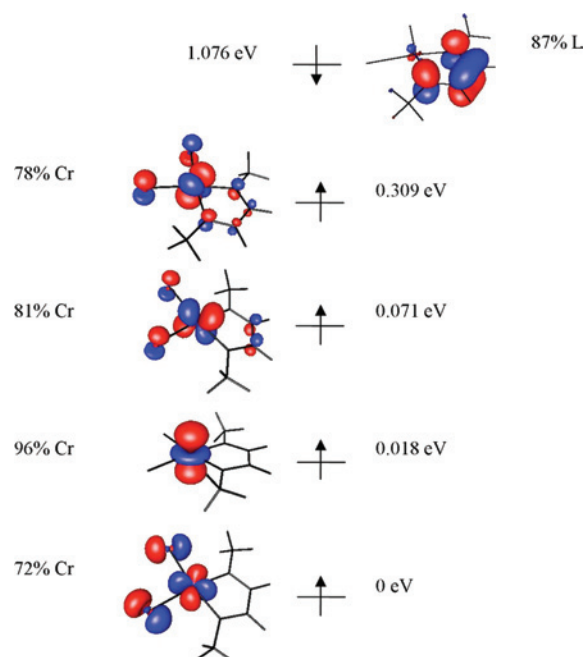
Figure 8. Qualitative MO diagram of **7′** showing the SOMOs (labeled with percentage of major contribution) that give rise to the $S = {}^3/_2$ spin state of **7**.

incrementally better description of both complexes acknowledges electron transfer from the metal to the easily reducible diimine ligands. As the assignment of an (integer) oxidation state of the metal is considered desirable and useful, a description most closely approximating the real distribution of the valence electrons is appropriate. For **7**, and **4**, that representation involves Cr(II) ions and diimine radical anions,
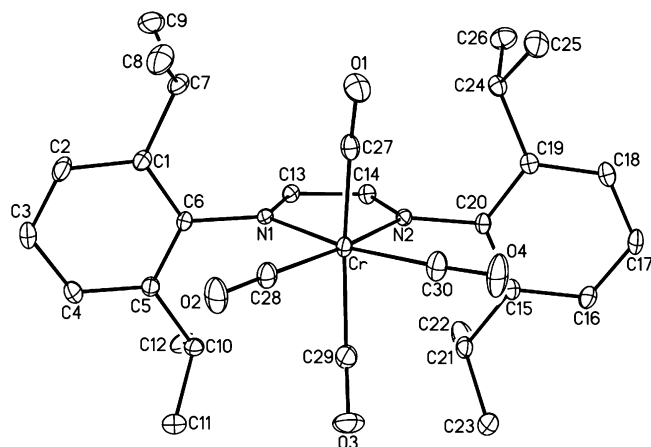
Figure 9. ORTEP plot of (^{H}L^{iPr})Cr(CO)$_4$ (**8**) at the 30% probability level. Hydrogen atoms have been omitted for clarity.

with strong antiferromagnetic coupling between the two. For dinuclear **4**, one consequence is that the weak magnetic coupling between the metal centers should be modeled assuming quartet ground states ($S = 3/2$) of the two interacting halves of the dimer. The apparent success of this end justifies the means.

To further explore the electron accepting nature of diimine ligands, we have synthesized the octahedral tetracarbonyl complex (^{H}L^{iPr})Cr(CO)$_4$ (**8**), the assignment of which as a Cr(0) diimine complex should be noncontroversial (see Figure 9 and Table 7 for the structure determination).[29] The C−N and C−C bond distances of the diimine ligand in **8** effectively split the difference between those in the free (neutral) ligand and the radical anion (see Table 6), while the CO stretching frequencies in the IR spectrum of **8** reveal a blue shift from $\nu_{CO,ave} = 1913$ cm^{-1} in the starting material, Cr(CO)$_4$(NCCH$_3$)$_2$, to $\nu_{CO,ave} = 1932$ cm^{-1} in **8**. This shift indicates less back-bonding from the metal to the CO ligands in **8** than in the starting material. Presumably, the diimine ligand is effectively competing with the CO ligands as a π-acid, being reduced to some extent. The "real" oxidation state of chromium in **8** is left for the reader to ponder.

Conclusion

We have prepared several chromium diimine complexes in *formal* oxidation states of the metal ranging from II to -I. These apparently low-valent complexes are stabilized by the electron-withdrawing nature of the diimines. We have shown that the π-acidity of these ligands allows for redistribution of electron density from the Cr center to the diimine ligand. The extent of reduction of the diimine ligands in the complexes varies anywhere between slight and approaching transfer of two electrons. The concomitant oxidation of the metal center creates some conceptual discomfort, as the assignment of metal oxidation state is no longer trivial. It is well to remember that the very concept of the latter is an (over)-simplification—integer numbers cannot capture the minute shifts of electron density engendered by charge, coordination number, geometry, coligands, and so forth.

(29) tom Dieck, H.; Kuehl, E. *Z. Naturforsch. B* **1982**, *37B*, 324.

Table 7. Selected Interatomic Distances (Å) and Angles (°) for One of the Two Independent Molecules of (^{H}L^{iPr})Cr(CO)$_4$ (**8**)

Distances (Å)					
Cr−N(1)	2.051(2)	Cr−N(2)	2.049(2)	Cr−C(27)	1.890(2)
Cr−C(28)	1.863(2)	Cr−C(29)	1.911(2)	Cr−C(30)	1.865(2)
N(1)−C(13)	1.298(3)	N(2)−C(14)	1.297(3)	C(13)−C(14)	1.433(3)

Angles (°)					
N(1)−Cr−N(2)	75.78(6)	N(1)−Cr−C(27)	97.54(8)	N(1)−Cr−C(28)	93.70(8)
N(2)−Cr−C(29)	97.83(8)	N(2)−Cr−C(30)	93.11(8)	C(27)−Cr−C(29)	158.4(1)
C(28)−Cr−C(30)	97.5(1)				

However, to the inorganic, and especially coordination chemist, oxidation state (along with d^n configuration) is a powerful predictive device. It is therefore defensible, and even profitable, to utilize a variety of experimental and computational techniques to "determine" the oxidation state that most closely reflects the electronic structure of any given compound. The result reported herein should be viewed in that context.

With these starting materials in hand and a grasp of their electronic structure in place, we plan to extend our preparative work to organometallic derivatives. We hope that in doing so we will be able to exploit the synergy between the metal and the diimine ligand and to discover interesting molecules and reactions. The first fruit of our labors, in the form of a Cr−Cr quintuple bond, has recently been communicated.[24] We believe that there is more where it came from.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk, vacuum line, and glovebox techniques. Pentane, diethyl ether, tetrahydrofuran, and toluene were distilled from purple Na benzophenone/ketyl solutions. THF-d_8 was predried over potassium metal and stored under vacuum over Na/K. CD$_2$Cl$_2$ was predried with P$_2$O$_5$ and stored under vacuum over 4 Å molecular sieves. C$_6$D$_6$ was predried with sodium metal and stored under vacuum over Na/K. CrCl$_3$ (anhydrous), CrCl$_2$ (anhydrous), and sodium metal were purchased from Strem Chemical Co., and Et$_4$NCl was purchased from Acros Organics. ((Trimethylsilyl)methyl) lithium was purchased as a 1 M solution in pentane from Aldrich, was crystallized from solution at −30 °C, and was isolated as a white crystalline solid. CrCl$_3$(THF)$_3$,[30] Cr(CO)$_4$(NCCH$_3$)$_2$ (**Caution! Pyrophoric**),[31] and all diimine ligands were prepared by literature procedures.[32] The synthesis of [(^{H}L^{iPr})Cr(μ-Cl)]$_2$ has been communicated recently.[24]

The AC susceptibility measurements were performed using the ACMS accessory for a Quantum Design PPMS (Physical Properties Measurement System).[33] The ACMS consists of a primary winding that causes the AC excitation field, as well as a pair of secondary windings. Each data point is the result of five measurements of the sample inside the instrument in a "five-point BTBCC (Bottom-Top-Bottom-Center-Center)" configuration. The samples were run at a constant field of 1 T.

NMR spectra were taken on a Bruker DRX-400 spectrometer and were referenced to the residual protons of the solvent (THF-

d_8, 1.73 and 3.58 ppm; CD$_2$Cl$_2$, 5.32 ppm; CDCl$_3$, 7.27 ppm). FTIR spectra were taken on a Mattson Alpha Centauri spectrometer with a resolution of 4 cm^{-1}. UV/vis spectra were taken on a Hewlett-Packard 8453 spectrophotometer. Elemental analyses were performed by Desert Analytics. Room-temperature magnetic susceptibility measurements were carried out using a Johnson Matthey magnetic susceptibility balance unless otherwise stated.

Preparation of [(^{H}L^{iPr})Cr]$_2$(μ-Cl)$_3$(Cl)(THF) (1′). To a slurry of CrCl$_2$ (0.034 g, 0.276 mmol) in THF (10 mL) was added 0.104 g of ^{H}L^{iPr} (0.276 mmol) at RT. The brown solution was allowed to stir overnight after which time the THF was removed, and the residue was crystallized from Et$_2$O at −30 °C to give **1** in 82% yield (0.121 g). ^{1}H NMR (CD$_2$Cl$_2$): 16.1 (br), 0.514 (br), −1.93 (br), −7.42 (br), −21.7 (vbr) ppm. ^{1}H NMR (THF-d_8): 20.028 (2H, aromatic), 0.217 (12H, iPr), −1.978 (12H, iPr), −10.274 (4H, iPr) ppm. IR (KBr; cm^{-1}): 3055 (m), 2946 (s), 2923 (s), 2863 (s), 1460 (s), 1443 (s), 1381 (m), 1359 (m), 1321 (m), 1248 (m), 1220 (m), 1175 (w), 1107 (w), 856 (m), 798 (m), 755 (m). Anal. Calcd. for C$_{56}$H$_{80}$N$_4$Cr$_2$Cl$_4$O: C, 62.79; H, 7.54; N, 5.23. Found: C, 62.65; H, 7.47; N, 5.00. UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 550 (2507), 638 (1067). μ_{eff} (294 K) = 3.9 (1) μ_B or 2.8(1) μ_B per Cr. Mp: 192 °C dec.

Preparation of (^{Me}L^{Me})CrCl$_2$(THF)$_2$ (2). To a slurry of CrCl$_2$ (0.067 g, 0.545 mmol) in THF (10 mL) was added 0.159 g of ^{Me}L^{Me} (0.545 mmol) at RT. The brown solution was allowed to stir overnight after which time the THF was concentrated and cooled to −30 °C overnight to give **2** in 42% yield (0.128 g) after washing with pentane. ^{1}H NMR (THF-d_8): 16.4 (2H, aromatic), −6.66 (12H, aryl Me), −9.52(6H, backbone Me) ppm. IR (KBr; cm^{-1}): 3011 (w), 2962 (s), 2931(s), 1465 (s), 1426 (m), 1377 (m), 1309 (w), 1257 (w), 1221 (s), 1162 (w), 1095 (w), 987 (w), 765 (m). UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 551 (304), 641 (229). Mp: 188 °C dec. Elemental analysis and magnetic measurements were not performed because of the inability to separate this complex from CrCl$_2$ produced by an, as of yet, uncharacterized ligand dissociation equilibrium.

Preparation of (^{H}L^{Me})CrCl$_2$(THF)$_2$ (3). To a slurry of CrCl$_2$ (0.048 g, 0.390 mmol) in THF (10 mL) was added 0.103 g of ^{H}L^{Me} (0.390 mmol) at RT. The brown solution was allowed to stir overnight after which time the THF was concentrated and cooled to −30 °C overnight to give **3** in 77% yield (0.160 g) after washing with pentane. ^{1}H NMR (THF-d_8): 21.0 (2H, aromatic), −11.1 (12H, aryl Me) ppm. IR (KBr; cm^{-1}): 3053 (m), 2946 (s), 2925 (s), 2855 (m), 1460 (s), 1444 (s), 1380 (m), 1357 (m), 1258 (m), 1234 (s), 1179 (w), 1097 (w), 1017 (m), 915 (w), 878 (m), 859 (m), 768 (m). Anal. Calcd. for C$_{26}$H$_{36}$N$_2$CrCl$_2$O$_2$: C, 58.75; H, 6.84; N, 5.27. Found: C, 58.67; H, 6.51; N, 5.34. UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 550 (832), 644 (356). μ_{eff} (294 K) = 2.9(1) μ_B. Mp: 200 °C dec.

Preparation of (^{H}L^{iPr})$_2$Cr (5). Solid Na (0.029 g, 1.261 mmol) was added to a THF (25 mL) solution of ^{H}L^{iPr} (0.469 g, 1.245 mmol). After stirring for 1 day, the deep red solution was slowly added to 0.075 g of CrCl$_2$ (0.610 mmol) suspended in 5 mL of THF. The reaction was allowed to stir at RT overnight. The resulting

(30) Herwig, W.; Zeiss, H. H. *J. Org. Chem.* **1958**, *9*, 1404.
(31) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.
(32) (a) tom Dieck, H.; Svoboda, M.; Greiser, T. *Z. Naturforsch. B* **1981**, *36B*, 823. (b) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523.
(33) For details see: http://www.qdusa.com/products/ppms.html (accessed April 16, 2008).

Table 8. Crystallographic Data for **1**−**3** and **5**−**8**

	1′	2	3	5	6	7	8
formula	$C_{63}H_{97.5}Cl_4-Cr_2N_4O_{2.75}$	$C_{28}H_{40}Cl_2-CrN_2O_2$	$C_{26}H_{36}Cl_2-CrN_2O_2$	$C_{52}H_{72}-CrN_4$	$C_{68}H_{106}Cr-LiN_4O_4$	$C_{38}H_{66}Cl_2-CrN_3O$	$C_{30}H_{36}Cr-N_2O_4$
fw	1200.75	559.52	531.47	805.14	1102.51	703.84	540.61
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
color	green	brown	brown	red	green	green	blue
a, Å	15.3679(15)	8.231(5)	9.533(2)	24.802(10)	22.054(9)	11.389(8)	10.908(3)
b, Å	40.969(4)	11.436(7)	22.328(5)	9.081(3)	13.047(5)	17.618(12)	13.495(4)
c, Å	22.124(2)	15.594(9)	12.676(3)	22.496(9)	23.299(9)	22.492(16)	20.150(6)
α, deg	90	77.112(8)	90	90	90	70.338(11)	90
β, deg	108.121(2)	78.381(9)	105.701(3)	112.71(1)	103.602(6)	81.626(12)	100.339(3)
γ, deg	90	82.698(8)	90	90	90	77.203(12)	90
V, Å^3	13239(2)	1396.3(14)	2597.6(10)	4674(3)	6516(4)	4132(5)	2918.0(14)
Z, Z'	8, 2	2, 1	4, 1	4, 1/2	4, 1	4, 2	4, 1
D(calcd), g cm^{-3}	1.205	1.331	1.359	1.144	1.124	1.131	1.231
μ(Mo Kα), mm^{-1}	0.533	0.628	0.672	0.283	0.223	0.436	0.427
temp, K	120	120	120	120	120	120	120
no. data/params	11 185/988	19 82/161	15 1/76	13 91/152	19 41/45	22 769/811	17 7/57
GOF on F^2	1.078	1.021	1.037	1.047	1.070	1.014	1.015
$R(F)$, %^{a}	4.61	4.29	6.50	8.53	7.92	5.81	4.23
$R_w(F^2)$, %^{a}	7.61	4.46	7.66	10.64	9.71	11.28	5.72

^{a} Quantity minimized: $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |F_o - F_c|$.

brown solution was filtered and washed with copious amounts of THF followed by solvent removal. The crude material was washed with Et$_2$O and dried under vacuum to give **5** in 67% yield (0.333 g). Crystals of **5** can be grown from concentrated THF solutions at −30 °C. ^{1}H NMR (THF-d_8): 16.6 (8H, aromatic), 0.11 (24H, iPr), −1.70 (24H, iPr), −11.4 (8H, iPr), −14.2 (4H, aromatic) ppm. IR (KBr; cm^{-1}): 3058 (w), 2959 (s), 2920 (m), 2866 (m), 1458 (m), 1438 (s), 1382 (w), 1360 (w), 1315 (m), 1250 (m), 1220 (m), 1178 (w), 1097 (w), 797 (m), 755 (m). Anal. Calcd. for C$_{52}$H$_{72}$N$_4$Cr: C, 77.56; H, 9.03; N, 6.46. Found: C, 77.40; H, 8.96; N, 6.72. UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 510 (4000), 730 (3297). μ_{eff} (300 K) = 2.7(1) μ_B (1 T, PPMS). Mp: 189 °C dec.

Preparation of Li(THF)$_4$[(^{H}L^{iPr})$_2$Cr] (6). A THF (20 mL) solution of **5** (0.180 g, 0.224 mmol) was cooled to −30 °C after which 0.031 g (0.330 mmol) of LiCH$_2$SiMe$_3$ was added. The green solution was allowed to stir for 2 h. The THF was removed, and the crude material washed with pentane, taken up in Et$_2$O and filtered. The filtrate was concentrated, layered with pentane, and cooled to −30 °C to give **6** in 71% yield (0.175 g). ^{1}H NMR (THF-d_8): 15.5 (8H, aromatic), 10.2 (24H, iPr), 1.73 (24H, iPr), −6.28 (8H, iPr), −7.47 (4H, aromatic) ppm. IR (KBr; cm^{-1}): 3049 (w), 2954 (s), 2922 (m), 2866 (w), 1544 (m), 1459 (s), 1431 (s), 1376 (m), 1314 (s), 1245 (s), 1205 (m), 1178 (s), 1112 (m), 1041 (s), 886 (w), 846 (w), 798 (w), 756 (m). Anal. Calcd. for C$_{68}$H$_{104}$N$_4$CrO$_4$Li: C, 74.20; H, 9.54; N, 5.09. Found: C, 72.31; H, 8.96; N, 5.52. UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 492 (1029), 741 (1464). μ_{eff} (300 K) = 3.9(1) μ_B (1 T, PPMS). Mp: 119 °C dec. Elemental analysis consistently gave results that were low in carbon and hydrogen content and high in nitrogen content. This is presumably due to decomposition of the lithium coordinated THF. Cation exchange with Et$_4$NCl produced an intractable material that could not be purified.

Preparation of Et$_4$N[(^{H}L^{iPr})CrCl$_2$] (7). To a THF (20 mL) solution of **4** (0.319 g, 0.688 mmol) was added 0.342 g (2.065 mmol) of Et$_4$NCl. The solution was allowed to stir overnight. The THF was then removed, and the crude material taken up in Et$_2$O and filtered. The green filtrate was concentrated and cooled to −30 °C to give **7** in 88% yield (0.381 g). ^{1}H NMR (THF-d_8): 18.6 (2H, aromatic), 1.01 (24H, iPr), −20.8 (4H, iPr) ppm. IR (KBr; cm^{-1}): 3050 (w), 2957 (s), 2927 (m), 2862 (m), 1655 (w), 1441 (s), 1393 (w), 1358 (w), 1321 (m), 1254 (s), 1219 (m), 1174 (m), 1102 (w), 1055 (w), 1000 (w), 797 (m), 758 (m). Anal. Calcd. for C$_{34}$H$_{56}$N$_3$CrCl$_2$: C, 64.84; H, 8.98; N, 6.67. Found: C, 64.64; H,

8.62; N, 6.56. UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 492 (4684), 632 (5588). μ_{eff} (294 K) = 3.9(1) μ_B. Mp: 178 °C dec.

Preparation of [(^{H}L^{iPr})Cr(CO)$_4$] (8). To a THF (20 mL) solution of 0.104 g of Cr(CO)$_4$(NCCH$_3$)$_2$ (0.423 mmol) was added 0.160 g (0.426 mmol) of ^{H}L^{iPr}. The resulting blue solution was allowed to stir overnight. The THF was then removed, and the crude material taken up in pentane. The pentane was concentrated and cooled to −30 °C to give **8** in 81% yield (0.186 g). ^{1}H NMR (CDCl$_3$): 8.050 (s, 2H, backbone), 7.217 (m, 6H, aromatic), 2.787 (m, 4H, iPr) 1.314 (d, 12H, iPr), 1.064 (d, 12H, iPr) ppm. IR (KBr; cm^{-1}): 3060 (w), 2964 (s), 2924 (m), 2865 (w), 2004 (vs), 1933 (vs), 1905 (vs), 1885 (vs), 1655 (w), 1436 (s), 1359 (w), 1323 (w), 1306 (w), 1178 (w), 1047 (w), 754 (w), 622 (m), 612 (m). Anal. Calcd. for C$_{30}$H$_{36}$N$_2$CrO$_4$: C, 66.65; H, 6.71; N, 5.18. Found: C, 66.24; H, 6.71; N, 5.19. UV/vis (THF; λ_{max}, nm (ε, M^{-1}cm^{-1})): 608 (6211). Mp: 98 °C dec.

Crystallographic Structure Determinations. A summary of crystal data collection and refinement parameters for compounds **1′**−**3** and **5**−**8** can be found in Table 8. Suitable crystals were selected, mounted with viscous oil and cooled to 120 K. Data were collected on a Bruker-AXS APEX CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 nm). Unit cell parameters were obtained from three sets of 20 frames using 0.3° ω scans from different sections of the Ewald sphere. Data sets were corrected for absorption using SADABS multiscan methods.[34] No symmetry higher than triclinic was observed for complexes **2** and **7**. Systematic absences in the diffraction data and unit cell parameters are consistent with $P2_1/n$ for complexes **1′**, **3**, **6**, and **8**. The C-centered space group $C2/c$ was found to be consistent for complex **5**. In all of the structures, the centrosymmetric space group options yielded chemically reasonable and computationally stable results of refinement. Structures were solved using direct methods and refined with full-matrix least-squares methods based on F^2. Two symmetry unique but chemically similar molecules are located in the asymmetric unit for complexes **1′** and **7**. Two structures display cocrystallized solvent molecules: **1′** has 1.75 molecules of disordered Et$_2$O per asymmetric unit that have been modeled as diffuse contributions,[35] and **7** has a Et$_2$O molecule per asymmetric unit. Except for compound **3**, the isopropyl moieties

(34) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
(35) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

display varied degrees of unresolvable disorder resulting in large *Ueq* ranges, and apparent Hirshfeld test failures. Complex **5** suffers severe disorder including a disordered diimine backbone that has been modeled such that the C−C and C−N bond distances are chemically reasonable. Various attempts to grow crystals in other solvents all resulted in the same disorder. Compound **8** consistently deposits as weakly diffracting, multiple crystals resulting to less than ideal data coverage. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions. All structure factors are included in the SHELXTL program library.[34] Details of crystal structure data are available from the Cambridge Structural Database under depository numbers: **1′**, 644255; **2**, 644260; **3**, 644263; **5**, 644257; **6**, 644258; **7**, 644262; **8**, 644256; and [($^H L^{iPr}$)Cr(μ-Cl)]$_2$(THF) (i. e., **4·THF**), 644259.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**−**3**, **5**−**8**, full structural data for **4·THF**, the details of the DFT calculations of **5′**, **6′** and **7′**, and the complete citation for the Gaussian 03 software package (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC800302W