2180 *Organometallics* **2010,** *29,* 2180–2185
DOI: 10.1021/om100144y

ORGANOMETALLICS
Article

Chromium(III) Bis(diketiminate) Complexes

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Received February 24, 2010

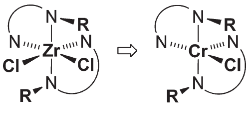
Reaction of two equivalents of the lithium salt of *N*,*N*′-dibenzyl-2-amino-4-iminopent-2-ene, *nacnac*^{Bn}Li(THF), **1**, with $CrCl_3(THF)_3$ or $CrCl_3$ yielded *nacnac*$^{Bn}{}_2$CrCl as a putative intermediate, which could be trapped by addition of 2,6-xylyl isocyanide to give the isocyanide-coordinated, octahedral complex *nacnac*$^{Bn}{}_2$CrCl($CNC_6Me_2H_3$), **5**. In the absence of isocyanide, ligand redistribution to the homoleptic tris(diketiminate) complex *nacnac*$^{Bn}{}_3$Cr, **3**, occurred upon concentration, standing, or workup with apolar solvents. Workup with diethyl ether afforded the bimetallic-bridged complex *nacnac*$^{Bn}{}_2$Cr(μ-Cl)$_2$Li(THF)$_2$, **6**. Reaction of $CrCl_3(THF)_3$ with one equivalent of **1** afforded the monodiketiminate complexes {*nacnac*^{Bn}CrCl(THF)(μ-Cl)}$_2$ or {*nacnac*^{Bn}CrCl(μ-Cl)}$_2$, depending on reaction conditions. Reaction of $CrCl_2(THF)_x$ with two equivalents of **1** gave rise to *nacnac*$^{Bn}{}_2$Cr, **4**. Complexes **3**–**6** were characterized by X-ray diffraction studies. All octahedral complexes display a *cis* geometry with two *nacnac* ligands in a distorted, boat-like conformation.

Introduction

Octahedral bis(diketiminate) complexes, *nacnac*$_2$M(X/L)$_2$, seem to fulfill several requirements of a successful catalytic system: a (reasonably) rigid ligand framework, a C_2-symmetric *cis* geometry, and an economical and easily modifiable spectator ligand (*nacnac*).[1] Recently, we have found that bis(diketiminate) zirconium complexes, *nacnac*$^{R}{}_2$ZrCl$_2$, where R = CH$_2$Ph, Cy, or *S*-CH(Me)Ph,[2] do not undergo chloride exchange with reagents such as LiR, MeMgBr, AlR$_3$, or NaOEt, unless one diketiminate ligand is partially dissociated. We speculated that moving from a Zr(IV) to a Cr(III) metal center will relieve the need for the second ancillary anionic ligand and that the open coordination site on the metal center will render the chloride ligand more susceptible to exchange (Scheme 1).

Evidence for bis(diketiminate) chromium complexes in the literature is limited to Theopold's work on *nacnac*$^{Ph}{}_2$Cr and *nacnac*$^{Ph}{}_2$CrX (X = Cl, Ph).[3] The crystal structure of the latter complex (X = Ph) displayed the targeted structure (Scheme 1): a square-pyramidal complex with an empty coordination site in *cis* position to the ancillary ligand. Possible modifications of the ligand in *nacnac*$^{Ph}{}_2$CrX are limited, however. Substitution of the N-phenyl substituents in *ortho* position prevents the coordination of two diketiminate ligands, and consequently, reactions of the commonly used *nacnac*^{dipp} or *nacnac*^{Xyl} ligands (dipp = 2,6-diisopropylphenyl, Xyl = 2,6-dimethylphenyl), for example, with $CrCl_3(THF)_3$ or $CrCl_2(THF)_x$ yielded only the monosubstituted complexes {*nacnac*CrCl(μ-Cl)}$_2$ or {*nacnac*Cr(THF)(μ-Cl)}$_2$.[4,5]

Scheme 1



Coordination of more than one ligand to chromium is achieved only if one N-Xyl or N-dipp group is replaced by less bulky groups, such as oxygen (*acnac*) or pyrrolide.[5−7] Alternatively, *nacnac*^{dipp} can be combined with a less encumbered ligand, such as acetylacetonate (*acac*), to afford *nacnac*^{dipp}(*acac*)CrCl.[8] However, reduction of steric hindrance enables the planar coordination of both ligands, with the two ancillary ligands (or the ancillary ligand and the open coordination site) *trans* to each other.[5,7−9] We have recently found that employing diketiminate ligands with N-alkyl instead of N-aryl substituents allows the coordination of two *nacnac* ligands in octahedral zirconium complexes. Although the complexes undergo a Bailar-twist isomerization in solution, NMR spectroscopy showed that the *trans* isomer was not accessible, even as a short-lived intermediate at elevated temperatures.[2] We present in the following our attempts to prepare *nacnac*$^{Bn}{}_2$CrCl(L) complexes (Bn = CH$_2$Ph), which should show the same preference for *cis* geometries as observed in the Zr complexes, but will hopefully enable easier exchange of the chloride ligand.

Results and Discussion

Reaction of 2 equiv of *nacnac*^{Bn}Li(THF), **1**, with $CrCl_3(THF)_3$ in toluene/THF (20:1) at room temperature afforded, after removal of LiCl by filtration, a green solution. Evaporation

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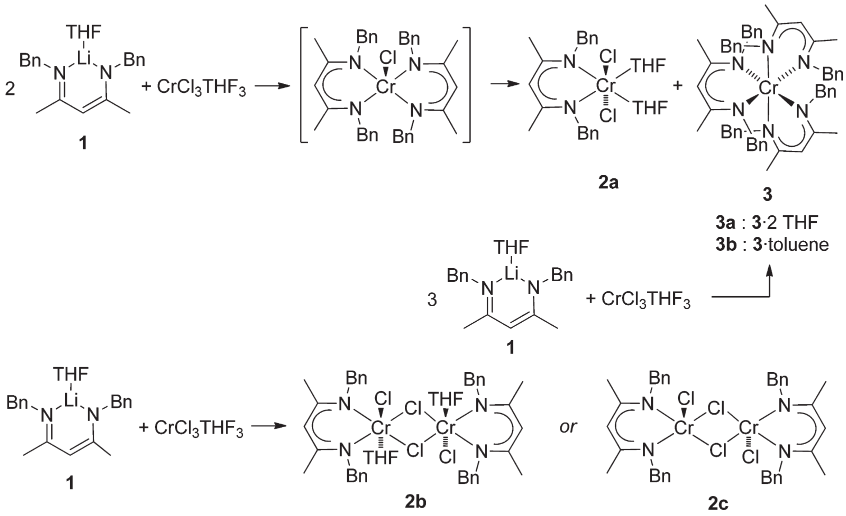
Scheme 2



and extraction with hexane yielded a hexane-insoluble, apple-green residue, **2a** (*vide infra*). From the hexane solution olive-green crystals were obtained. X-ray diffraction analysis identified the latter to be not the expected product $nacnac^{Bn}{}_2CrCl(THF)_{0-1}$, but the homoleptic complex $nacnac^{Bn}{}_3Cr\cdot 2THF$, **3a** (Scheme 2). Complex **3a** was also prepared independently from 3 equiv of **1** and $CrCl_3(THF)_3$ in 90% yield. Under modified reaction conditions (co-evaporation with toluene), crystals of **3** incorporated co-crystallized toluene to give $nacnac^{Bn}{}_3Cr\cdot C_7H_8$, **3b**. Despite the multitude of trisacetylacetonate metal complexes, only selected examples of homoleptic tris(diketiminate) complexes are known. Thus, preparation of tris($nacnac^{Ar}$)Ln has been reported for several lanthanides, where increased M−N bond lengths allow the coordination of three diketiminate ligands.[10] With aliphatic substituents on nitrogen, synthesis of $nacnac^{Et}{}_3M$ (M = Al, Ti, and Cr) has been reported in the patent literature, although the compounds were not characterized,[11] while Kuhn et al. isolated $nacnac^{Me}{}_3Al$.[12]

The crystal structures of **3a** and **3b** differ only in the nature of the co-crystallized solvent, which does not show any interaction with the complex, and in that **3b** crystallizes on a crystallographic C_2 axis. In the margin of errors, geometrical parameters of both structures were nearly identical. In both **3a** and **3b** (Figure 1) two diketiminate ligands adopt the typical boat-like distortion of κ^2-coordinated diketiminates, with the metal bent out of the mean ligand plane by 35° (**3a**) and 37° (**3b**) and both phenyl groups in a *syn* orientation on the same side of the ligand. The third diketiminate ligand has both phenyl groups in an *anti* orientation, and the metal center is situated in the mean ligand plane. Cr−N distances are slightly longer and the N−Cr−N bite angle slightly larger in the latter ligand. Out-of-plane coordination of the chromium center with *syn*-oriented substituents seems thus preferable to in-plane coordination with the substituents in *anti* position. The same coordination geometry, i.e., two ligands with a boat-like distortion and one ligand with the metal in the mean ligand plane, a slightly increased N−M−N bite angle, and increased metal−nitrogen distances, was observed in the crystal structure of $nacnac^{Me}{}_3Al$.[12]

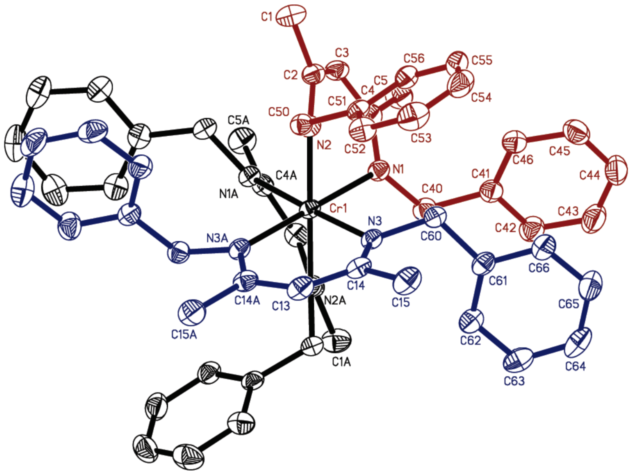


Figure 1. Crystal structure of **3b**. (The structure of **3a** is nearly identical and not shown.) Hydrogen atoms and disordered solvent molecule were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

We were unable to obtain single crystals of the hexane-insoluble precipitate **2a**, obtained in the reactions that yielded **3**. Its elemental analysis was in reasonable agreement with an assignment as $nacnac^{Bn}CrCl_2(THF)_2$, **2a** (Scheme 2). Attempts to prepare **2a** independently under similar conditions yielded the corresponding compounds **2b** and **2c**, with one or no coordinated THF molecule per metal center, respectively (Scheme 1), which are probably present as chloride-bridged dimers.[5,8] Kim et al. obtained the related compound $nacnac^{Ph}CrCl_2(THF)_2$ from crystallization in THF and reported THF binding−dissociation equilibria for this complex.[13] Although the assignment of **2a** remains tentative, elemental analysis data and its magnetic moment suggest the presence of a chromium(III) complex with one coordinated diketiminate ligand.

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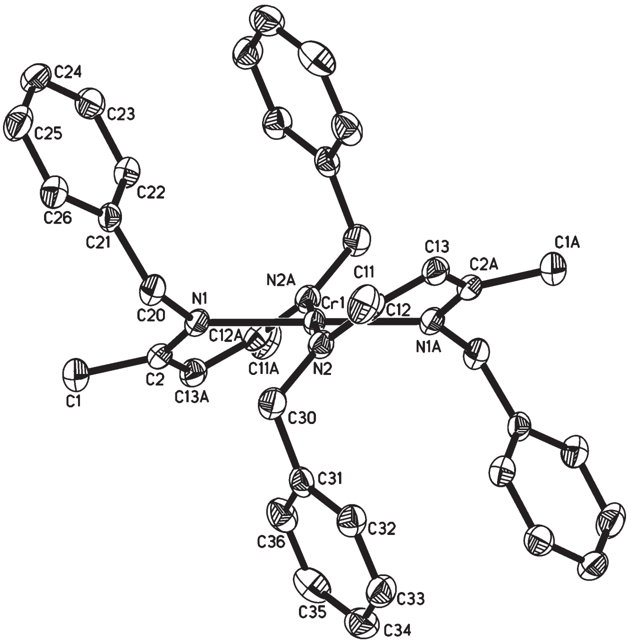
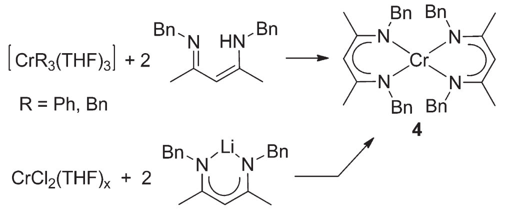


Figure 2. Crystal structure of **4**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 3



Variation of the reaction conditions (solvent, temperature) or the starting material (CrCl$_3$(THF)$_3$ or CrCl$_3$) did not influence the outcome of the reaction, and we consistently obtained insoluble precipitates and the hexane-soluble tris(diketiminate) adduct **3**, in the form of either **3a** or **3b** (identified in most cases by X-ray diffraction and/or elemental analysis). Reactions of the diketimine *nacnac*$^{\mathrm{Bn}}$H with CrPh$_3$ or CrBn$_3$, prepared *in situ*, led to reduction of the metal and afforded the homoleptic Cr(II) complex **4** (Scheme 3), which can also be prepared independently from CrCl$_2$(THF)$_x$ and **1**. In contrast to *nacnac*$^{\mathrm{Ph}}{}_2$Cr,[3] attempts to oxidize **4** to *nacnac*$^{\mathrm{Bn}}{}_2$CrCl under a variety of conditions (including addition of 2,6-xylyl isonitrile prior to crystallization) did not yield any identifiable products.

The crystal structure of **4** shows the chromium center in a square-planar coordination with the metal atom on a crystallographic inversion center (Figure 2, Table 1). The bite angle of the diketiminate ligand (86.30(5)°) is comparable to those observed in **3a** and **3b** (84.63(5)−85.31(9)°) and causes the N−Cr−N angle between the two diketiminate ligands to be slightly larger than 90° (93.70(5)°). Both diketiminate ligands show a boat-like distortion with the metal center bent by 36° out of the mean ligand plane, which can be attributed to the unfavorable in-plane interactions of the N-alkyl substituents. The structure of **4** is similar to that observed for *nacnac*$^{i\mathrm{Pr}}{}_2$Pd,[14] but notably different from the only other reported bis(diketiminate) chromium(II) complex, *nacnac*$^{\mathrm{Ph}}{}_2$Cr,[3] which shows a severely distorted planar geometry with a 57° angle between the (Cr/N/N) planes of the two diketiminate ligands. As we have noted before for other metal complexes,[2,15] diketiminates with primary alkyl substituents on nitrogen provide significantly less congested coordination environments than ligands with N-aryl substituents.

During reactions of CrCl$_3$(THF)$_3$ with **1** described above, changes observed in the solubility of compounds seemed to indicate that a *nacnac*$^{\mathrm{Bn}}{}_2$CrCl species was indeed obtained at some point of the reaction and underwent ligand redistribution to **2** and **3** upon concentration or standing. Evidence for the intermediate formation of *nacnac*$^{\mathrm{Bn}}{}_2$CrCl came from the treatment of the reaction mixture of **1** and CrCl$_3$(THF)$_3$ with xylyl isocyanide prior to concentration, which afforded the isocyanide-coordinated compound **5** in 72% yield after crystallization (Scheme 4). In its structure (Figure 3, Table 1), the chloride and the isocyanide ligand replaced the diketiminate ligand found with a *trans* orientation of the phenyl rings in **3a** or **3b**, in agreement with its weaker coordination indicated in the structures of **3a** and **3b** (*vide supra*). The two remaining diketiminate ligands again show a boat-like distortion with phenyl rings in a *syn* orientation on one side of the mean ligand plane. The ligand distortion places the benzylic carbon atoms (C20, C50, Figure 3) between the chloride and the isocyanide ligand, instead of being eclipsed with the Cr−Cl or Cr−C60 bond. In this, the structure of **5** is very similar to the corresponding *nacnac*$^{\mathrm{Bn}}{}_2$ZrCl$_2$ complex.[2] Due to the mediocre crystal quality in the X-ray diffraction study of **5**, we refrain from a more in-depth analysis of the structure.

Complex **5** shows a stretching frequency of $\nu_{\mathrm{CN}} = 2117\ \mathrm{cm}^{-1}$ in its IR spectra, practically unchanged from free isocyanide ($\nu_{\mathrm{CN}} = 2119\ \mathrm{cm}^{-1}$). The frequency is notably lower than in (C$_6$F$_5$S)$_3$Cr(CNXyl)$_3$ (ν_{CN} = 2183, 2330, and 2358 cm^{-1})[16] and comparable to those observed in Shapiro's *ansa*-chromocene complexes ([Me$_4$C$_2$(C$_5$H$_4$)$_2$Cr$^{\mathrm{III}}$(CNXyl)]$^+$: $\nu_{\mathrm{CN}} = 2119$ cm^{-1}, Me$_4$C$_2$(C$_5$H$_4$)(C$_5$H$_4$B(C$_6$F$_5$)$_3$)Cr$^{\mathrm{III}}$(CNXyl): $\nu_{\mathrm{CN}} = 2100$ cm^{-1}).[17,18] In contrast to these pseudotetrahedral chromocenes, for which coordination of isocyanide to a cationic, high-spin chromocene resulted in a low-spin isocyanide adduct,[18] octahedral **5** remains, as expected, a high-spin complex ($\mu_{\mathrm{eff}} = 3.5(1)\ \mu_{\mathrm{B}}$).

While **5** confirmed the intermediate formation of a bis(diketiminate) complex, the strong coordination of the isocyanide ligand prevents further modifications. Attempts to trap the intermediate product with pyridine or triphenylphosphine failed. Use of CrCl$_3$(py)$_3$ as starting material or reaction of the putative intermediate with NaO*t*Bu or BnMgBr, to replace chloride with a less easily exchangeable ligand, likewise did not yield any identifiable products. Reactions of **1** with CrCl$_3$(THF)$_3$ afforded in some cases batches whose elemental analysis proposed a composition of *nacnac*$^{\mathrm{Bn}}{}_2$Cr(μ-Cl)$_2$Li(THF)$_2$, **6**. Yields of this compound were, however, unreliable, and in most cases ligand redistribution to **2** and **3** occurred. Addition of

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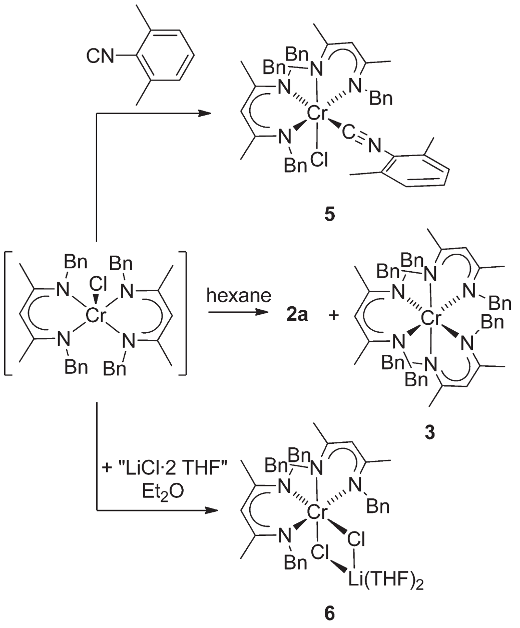
Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] for 3a, 3b, and 4−6

	3a	**3b**	**4**	**5**	**6**
Cr−N[a]	2.052(2)−2.083(2)	2.054(1), 2.110(1)	2.060(1), 2.059(1)	2.013(8)−2.054(8)	2.016(3)−2.060(3)
Cr−N[b]/Cr−Cl	2.104(2), 2.112(2)	2.116(1)		2.356(3), 2.365(3)	2.422(1), 2.430(1)
Cr−C				2.132(12), 2.142(14)	
N−Cr−N[c]	85.20(8) 85.31(9)	84.63(5)	86.30(5)	85.6(3)−86.4(3)	85.09(11), 85.30(11)
N−Cr−N[d]	89.91(9)	88.24(8)			
N−Cr−X[e]	85.76(9)−97.16(8)	85.62(8)−96.75(5)	93.70(5)	88.9(4)−94.0(2)	89.63(8)−93.84(8)
Cl−Cr−Y[f]				84.4(3), 85.0(3)	87.82(3)
bending angle[g]	0, 35, 35	0, 37	36	36−38	39, 40

[a] Diketiminate ligands with boat-like distortions (**3a**: N3−N6; **3b**: N1, N2). [b] Diketiminate ligand with Cr in the mean ligand plane (**3a**: N1, N2; **3b**: N3). [c] Bite angle of diketiminate ligands with boat-like distortion. [d] Bite angle of diketiminate ligands with in-plane metal coordination. [e] X = **3a**, **3b**, **4**: N atoms of a different ligand. **5**: N atoms of a different ligand, C60, C200, Cl1, Cl2. **6**: N atoms of a different ligand, Cl1, Cl2. [f] Y = **5**: C60, C200. **6**: Cl2. [g] Bending of the metal center out of the mean ligand plane, described by the angle between the (N1, N2, C2, C4) and the (Cr1, N1, N2) plane (numeration according to Figure 1).

Scheme 4



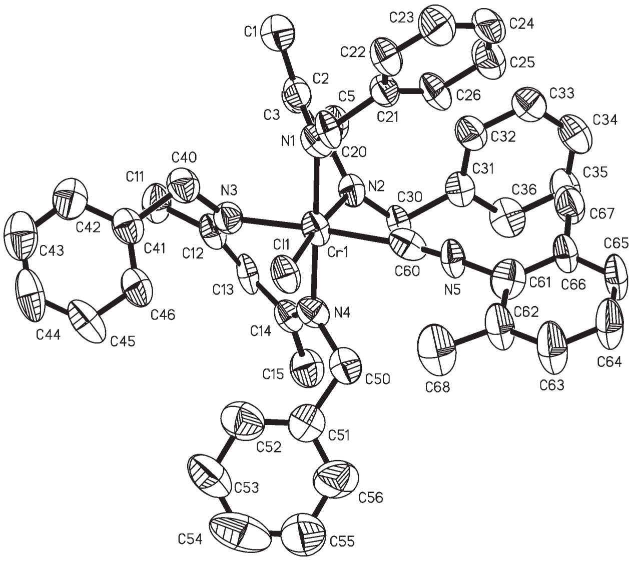


Figure 3. Crystal structure of **5**. Only one of two independent molecules in the unit cell is shown. Hydrogen atoms and cocrystallized diethyl ether were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

excess LiCl did not improve the yields of **6** or the reliability of the synthetic protocol. Change of the workup procedure to extraction with diethyl ether finally afforded **6** in 70% crystallized yield (Scheme 4).

The crystal structure of **6** (Table 1, Figure 4) confirms a chloride-bridged dinuclear complex, with chromium in an octahedral environment and two additional THF ligands complementing the coordination sphere of the lithium atom. The steric influence of the coordinated THF molecules is notable in a slightly greater boat-like distortion of the ligands (Table 1), i.e., an increased bending of the chromium center out of the mean ligand plane, but otherwise the structure is very similar to that of isocyanide-coordinated **5**.

It is notable that in contrast to *nacnac*$^{Bn}{}_2$CrCl its analogue with N-phenyl substituents, *nacnac*$^{Ph}{}_2$CrCl,[3] does not undergo a comparable ligand exchange. Taking into account the strong distortions observed in the crystal structure of *nacnac*$^{Ph}{}_2$Cr compared to the symmetrical *nacnac*$^{Bn}{}_2$Cr, the stability of *nacnac*$^{Ph}{}_2$CrCl might well be based on its inability to form the corresponding tris(diketiminate) complex.

Conclusions

The presented study was motivated by the lack of reactivity observed in *nacnac*$^{R}{}_2$ZrCl$_2$ complexes toward exchange of the chloride ligands. This was resolved by switching the central metal to Cr(III) and thus opening one coordination site. Complexes **5** and **6** show the targeted octahedral *nacnac*$^{Bn}{}_2$CrCl(L) geometry with isocyanide or μ-Cl occupying the free coordination site *cis* to chloride. As envisioned, chloride exchange became easier with Cr, as shown by the fast formation of homoleptic **3** from **1** and CrCl$_3$(THF)$_3$ at room temperature.

The crystal structures of **3a**, **3b**, **5**, and **6** displayed a common structural motif for the obtained *nacnac*$^{Bn}{}_2$CrX$_2$ complexes, consisting of two boat-like distorted, nearly coplanar diketiminate ligands. The N-alkyl substituents are found in a *syn* orientation, pointing away from the metal center, and placed directly above and below the *cis*-coordinated CrX$_2$ fragment. The essentially identical coordination of the diketiminate ligands observed in *nacnac*$^{Bn}{}_2$ZrCl$_2$, carrying the same ligand,[2] as well as in other *nacnac*$^{R}{}_2$MX$_2$ complexes (R = alkyl, phenyl, tolyl; M = Al, Ti, Zr),[2,12,19] appears to indicate that this geometry is a general motif for octahedral bis(diketiminate) metal complexes.

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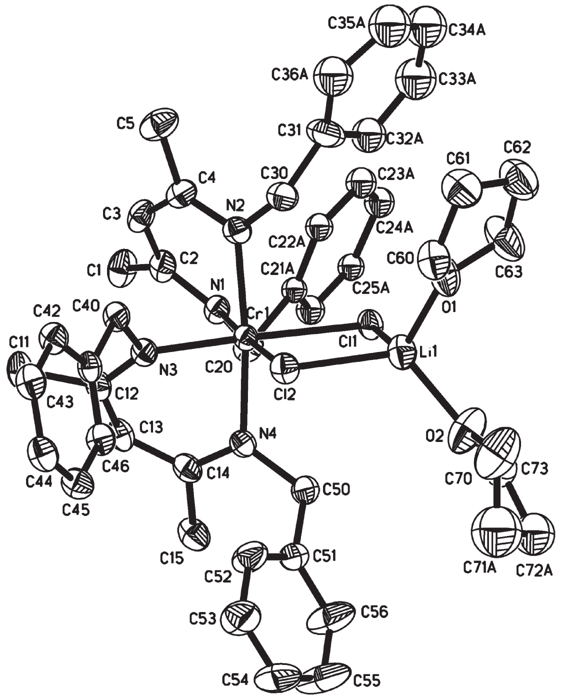

Figure 4. Crystal structure of **6**. Hydrogen atoms and disordered atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Bis(diketiminate) chromium complexes thus seem to be promising candidates for metal-assisted transformations: the two spectator ligands form a predictable, rigid, and easily modified C_2-symmetric coordination environment, and the reactive coordination sites are accessible to substrates.[20] Future efforts will concentrate on potential applications and to prevent the ligand redistribution to *nacac*$^{\mathrm{Bn}}{}_3$Cr, e.g., by bridging of the diketiminate ligands.

Experimental Section

All reactions, except ligand synthesis, were carried out under an inert atmosphere using Schlenk and glovebox techniques under a nitrogen atmosphere. *nacnac*$^{\mathrm{Bn}}$Li(THF) (**1**),[2] *nacnac*$^{\mathrm{Cy}}$Li(THF),[2] *S*,*S*-*nacnac*$^{\mathrm{CH(Me)Ph}}$Li(THF),[2] $CrCl_3(THF)_3$,[21] and $CrCl_2(THF)_x$[22] were prepared according to literature procedures. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and deoxygenated by repeated extraction with nitrogen. C_6D_6 was dried over sodium and degassed by three freeze−pump−thaw cycles. All others chemicals were purchased from common commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AMX 300 or Bruker AV 400 spectrometer. Chemical shifts were referenced to the residual signals of the deuterated solvents (C_6D_6: ^{1}H: δ 7.16 ppm, ^{13}C: δ 128.38 ppm). Magnetic susceptibility measurements were carried out at room temperature in grease-sealed capillaries on a Johnson Matthey magnetic susceptibility balance. Elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal). Absorption spectra were measured in dry solvent in a sealed cell at room temperature on a Cary 500i spectrophotometer.

Attempted Synthesis of *nacnac*$^{\mathbf{Bn}}{}_2$CrCl(THF). A solution *nacnac*$^{\mathrm{Bn}}$Li(THF), **1** (1 g, 2.80 mmol), in toluene (20 mL) was added to a suspension of $CrCl_3(THF)_3$ (0.5 g, 1.40 mmol) in toluene (20 mL). After the mixture was stirred for 12 h at room temperature, it was filtered to remove LiCl. The volatiles were removed, and the residue extracted with hexane (100 mL). Filtration yielded an apple-green powder, tentatively assigned to *nacnac*$^{\mathrm{Bn}}$$CrCl_2(THF)_2$, **2a** (500 mg, 65%). Anal. Calcd for $C_{27}H_{37}N_2O_2CrCl_2$: C, 59.56; H, 6.85; N, 5.14. Found: C, 60.72; H, 6.32; N, 5.19. μ_{eff}(298 K) = 4.2(1) μ_{B}.

Slow evaporation of the olive-green filtrate obtained above at room temperature yielded olive-green crystals of *nacnac*$^{\mathrm{Bn}}{}_3$Cr·2THF, **3a**, identified by X-ray diffraction analysis.

{*nacnac*$^{\mathbf{Bn}}$CrCl$_2$(THF)}$_2$, 2b. A solution of **1** (0.20 g, 0.56 mmol) in toluene (20 mL) was added dropwise to a solution of $CrCl_3(THF)_3$ (0.20 g, 0.53 mmol) in THF (5 mL) and toluene (20 mL). After stirring overnight at room temperature and filtration to remove LiCl, all volatiles were removed under vacuum. The residue was extracted with hexane, filtered, and, after evaporation of the filtrate, redissolved in a mixture of THF (5 mL) and hexane (10 mL). A final evaporation of the solvent yielded 0.20 g (79%) of an apple-green powder. Anal. Calcd for $C_{46}H_{58}N_4Cl_4Cr_2O_2$: C, 58.48; H, 6.19; N, 5.93. Found: C, 58.82; H, 6.29; N, 5.91. Mp: 146 °C.

{*nacnac*$^{\mathbf{Bn}}$CrCl$_2$}$_2$, 2c. A solution of **1** (0.300 g, 0.84 mmol) in toluene (20 mL) was added to a solution of $CrCl_3(THF)_3$ (0.200 g, 0.53 mmol) in toluene (30 mL), upon which the color of the latter changed from purple to green. After stirring overnight at room temperature and filtration to remove LiCl, the solvent was removed under vacuum and the residue extracted with hexane (20 mL). The olive-green powder isolated by filtration was washed several times with hexane and dried under vacuum to yield 0.200 g (93%) of **2c**. Anal. Calcd for $C_{19}H_{21}N_2CrCl_2$: C, 57.01; H, 5.29; N, 7.00. Found: C, 56.36; H, 5.61; N, 6.56. Mp: 160 °C.

***nacnac*$^{\mathbf{Bn}}{}_3$Cr·2THF, 3a.** A solution of **1** (1.0 g, 2.81 mmol) in toluene (20 mL) was added to a solution of $CrCl_3(THF)_3$ (0.35 g, 0.94 mmol) in toluene (30 mL), upon which the color of the solution changed from purple to green. After stirring overnight at room temperature and filtration to remove LiCl, the solvent was removed under vacuum and the residue was extracted with hexane (100 mL). Filtration and evaporation of the solvent yielded **3a** as an olive-green powder (0.89 g, 92%). Anal. Calcd for $C_{57}H_{63}N_6Cr\cdot 2C_4H_8O$: C, 75.92; H, 7.74; N, 8.17. Found: C, 75.29; H, 7.56; N, 8.25. Mp: 180 °C. Presence of 2 ± 0.3 equiv of THF was confirmed by NMR.

***nacnac*$^{\mathbf{Bn}}{}_3$Cr·C$_7$H$_8$, 3b.** A solution of **1** (0.41 g, 1.2 mmol) in toluene (15 mL) was added to a suspension of $CrCl_3(THF)_3$ (0.21 g, 0.6 mmol) in toluene (10 mL). After the mixture was stirred overnight at room temperature, it was filtered to remove LiCl. All volatiles were removed under vacuum, and the remaining residue was co-evaporated twice with toluene (2 × 25 mL) and washed twice with hexane (2 × 20 mL). Crystallization from toluene at −30 °C yielded olive-green needles of **3b** (300 mg, 58%). Anal. Calcd for $C_{57}H_{63}N_6Cr\cdot C_7H_8$: C, 78.74; H, 7.33; N, 8.61. Found: C, 77.70; H, 7.46; N, 8.46.[23] μ_{eff}(298 K) = 3.9(1) μ_{B}. UV/vis (toluene; λ, nm (ε, $M^{-1}\cdot cm^{-1}$)): 368 (1300), 414 (1300), 770 (550). Mp: 180 °C.

***nacnac*$^{\mathbf{Bn}}{}_2$Cr, 4. From Cr(II).** $CrCl_2(THF)_x$ (0.4 g, 1.68 mmol for x = 2) was dissolved in THF (30 mL), and a solution of **1**

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(20) In very preliminary attempts, we added methyl Grignard to reaction mixtures containing **6** and styrene. Small amounts (2−4%) of isopropylbenzene were found in the organic phase after aqueous work-up.

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(23) Elemental analyses for some compounds in this article showed low carbon values up to ΔC = 1%, despite the use of crystalline material suitable for single-crystal diffraction studies. Recrystallization did not improve on these values. Although we cannot explain this behavior and cannot exclude the presence of small amounts of impurities, slight variations toward low carbon values might indicate oxidation/hydrolysis during the measurement, which is performed under ambient conditions with samples prepared in a glovebox. We noted that MacAdams et al. reported similar deviations for *nacnac*$^{\mathrm{Ph}}$ chromium complexes (see ref 3).

Table 2. Details of X-ray Diffraction Studies

	3a[a]	**3b**	**4**	**5**	**6**
formula	$C_{57}H_{63}CrN_6$[a]	$C_{57}H_{63}CrN_6 \cdot C_7H_8$	$C_{38}H_{42}CrN_4$	$C_{47}H_{51}ClCrN_5 \cdot (C_4H_{10}O)_{0.25}$	$C_{46}H_{58}Cl_2CrLiN_4O_2$
M_w (g/mol); F(000)	884.13; 1884 [a]	976.27; 2084	606.76; 322	791.91; 1678	828.80
T (K); wavelength	150; 1.54178	150; 1.54178	150; 1.54178	150; 1.54178	150; 1.54178
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
unit cell: a (Å)	11.0625(6)	11.0133(3)	9.2442(4)	11.289(1)	13.928(2)
b (Å)	23.6978(13)	18.4416(5)	9.3053(4)	17.818(2)	29.976(4)
c (Å)	21.5716(11)	26.4697(6)	9.8732(4)	22.393(2)	11.357(1)
α (deg)			103.695(2)	86.836(4)	
β (deg)	92.399(2)	97.403(1)	98.265(2)	80.564(5)	110.141(6)
γ (deg)			101.495(2)	81.874(4)	
V (Å^3); Z	5650.2(5); 4	5331.3(2); 4	792.17(6); 1	4396.6(7); 4	4451.6(9); 4
$d_{calcd.}$ (g/cm^3)	1.039 [a]	1.216	1.272	1.196	1.237
θ range (deg); completeness	2.8−55.6; 0.98	3.4−67.8; 0.98	4.7−67.7; 0.98	2.0−60.2; 0.89	3.0−67.6; 0994
collected reflns; R_σ	69 584; 0.084	42 914; 0.045	11 177; 0.028	67 699; 0.180	61 562; 0.025
unique reflns; R_{int}	7129; 0.091	4732; 0.062	2812; 0.041	11673; 0.199	7990; 0.052
μ (mm^{-1}); abs corr	1.947; multiscan	2.111; multiscan	3.211; multiscan	2.987; multiscan	3.528; multiscan
R1(F); wR(F^2) ($I > 2\sigma(I)$)	0.040; 0.078	0.034; 0.083	0.035; 0.101	0.089; 0.232	0.060; 0.173
R1(F); wR(F^2) (all data)	0.073; 0.084	0.051; 0.087	0.035; 0.101	0.209; 0.303	0.069; 0.181
GoF(F^2)	0.85	0.95	1.02	0.954	1.02
residual electron density	0.15	0.20	0.35	1.05	0.62

[a] Co-crystallized solvent removed with SQUEEZE.

(1.2 g, 3.37 mmol) in THF (20 mL) was added. The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was extracted with diethyl ether (120 mL). The extract was filtered to remove LiCl, concentrated, and cooled to −30 °C to yield red crystals of *nacnac*$^{Bn}{}_2$Cr (0.90 g, 90% yield). Anal. Calcd for $C_{38}H_{42}N_4Cr$: C, 75.22; H, 6.98; N, 9.23. Found: C, 73.66; H, 7.14; N, 8.96.[23] μ_{eff}(298 K) = 4.1(1) μ_B. Mp: 152−155 °C.

From Cr(III). $CrCl_3$ (0.50 g, 3.2 mmol) was suspended in THF (40 mL) and cooled to −78 °C. A solution of PhLi in dibutyl ether (2.0 M, 5.0 mL, 10 mmol) was added dropwise, which caused an immediate color change to brown-red. After stirring for 5 h at −78 °C, a solution of *nacnac*^{Bn}H (2.1 g, 0.75 mmol) in THF (20 mL) was added. The reaction was allowed to warm to room temperature overnight. The solvent was removed *in vacuo*, and the residue was extracted with diethyl ether (100 mL). The extract was then filtered to remove LiCl, concentrated, and kept at −30 °C to yield red-purple crystals of *nacnac*$^{Bn}{}_2$Cr (0.51 g, 26%), identified by X-ray diffraction. Anal. Calcd for $C_{38}H_{42}N_4Cr$: C, 75.22; H, 6.98; N, 9.23. Found: C, 74.48; H, 7.00; N, 9.30.[23]

***nacnac*$^{Bn}{}_2$CrCl(CNC$_6$Me$_2$H$_3$), 5.** A solution of **1** (0.70 g, 2.0 mmol) in toluene (30 mL) was added to a suspension of $CrCl_3(THF)_3$ (0.34 g, 0.89 mmol) in toluene (40 mL). After stirring for 12 h at room temperature and filtration to remove LiCl, 2,6-dimethylphenyl isocyanide (0.175 g, 1.3 mmol) was added. The solution was stirred for additional 12 h and concentrated to 7 mL. Hexane (10 mL) was added and the solution left to stand overnight. The precipitate formed was eliminated by filtration, the volatiles were removed under vacuum, and the remaining solid was recrystallized from diethyl ether (10 mL) at −30 °C to yield **5** as green crystals (0.59 g, 72%). Anal. Calcd for $C_{47}H_{51}N_5ClCr \cdot (C_4H_{10}O)_{0.25}$: C, 72.80; H, 6.81; N, 8.84. Found: C, 72.89; H, 7.78; N, 8.31. IR (toluene): ν_{CN} = 2117 cm^{-1}. μ_{eff}(298 K) = 3.5(1) μ_B. Mp: 149 °C.

***nacnac*$^{Bn}{}_2$Cr(μ-Cl)$_2$Li(THF)$_2$, 6.** A solution of **1** (0.60 g, 1.7 mmol) in THF (20 mL) was added to a suspension of $CrCl_3(THF)_3$ (0.30 g, 0.80 mmol) in THF (20 mL). The reaction mixture was stirred overnight at room temperature, the solvent was evaporated, and the residue was extracted with diethyl ether (60 mL). After filtration to remove LiCl and concentration, the solution was placed at −30 °C, and brown crystals of **6** were obtained after several days (462 mg, 70% yield). Anal. Calcd for $C_{46}H_{58}N_4O_2LiCrCl_2$: C, 66.66; H, 7.05; N, 6.76. Found: C, 66.96; H, 6.90; N, 7.22. UV/vis (toluene; λ, nm (ε, M$^{-1}\cdot$cm^{-1})): 308 (14 000), 392 (6500), 761 (1900). μ_{eff}(298 K) = 3.4(1) μ_B. Mp: 158 °C.

X-ray Diffraction Studies. Crystals suitable for X-ray diffraction studies were obtained directly from the synthetic recrystallizations described above. Diffraction data were recorded on a Bruker Proteum X8/Microstar (Cu radiation), using the APEX2 software package.[24] Data reduction was performed with SAINT;[25] absorption corrections with SADABS.[26] Structures were solved with direct methods (SHELXS97).[27] All non-hydrogen atoms were refined anisotropically using full-matrix least-squares on F^2 and hydrogen atoms refined with fixed isotropic U using a riding model (SHELXL97).[27] For **3a**, the co-crystallized solvent was identified as disordered THF and suppressed by application of SQUEEZE.[28] Co-crystallized solvent in **3b** (toluene) and **5** (ether) and disorders of one isocyanide ligand in **5** and of the THF and two phenyl groups in **6** were modeled using appropriate restraints and refined isotropically in most cases. For further details see Table 2 and the Supporting Information.

Acknowledgment. Funding for this research was provided by the Natural Sciences and Engineering Research Council of Canada and the Université de Montréal. We thank Francine Bélanger for her support with the crystal structure determinations.

Supporting Information Available: Details of X-ray diffraction studies (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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