Organometallics **2002,** *21,* 952−960

The $(Ph)_2$nacnac Ligand in Organochromium Chemistry

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Received October 2, 2001

A novel class of β-diketiminato chromium complexes was prepared to serve as a homogeneous model system for the heterogeneous Phillips ethylene polymerization catalyst. $(Ph)_2nacnacCrCl_2(THF)_2$ (**1**, $(Ph)_2$nacnac = *N*,*N*′-diphenyl-2,4-pentanediimine anion) was found to polymerize ethylene in the presence of excess methylaluminoxane (MAO). Reaction of **1** with 1.0 equiv of an alkylzinc compound yielded dimeric, chloride-bridged monoalkyl complexes of the type $[(Ph)_2nacnacCrR(\mu\text{-}Cl)THF]_2$ (R = Me (**3a**), Et (**3b**)). Reaction of **1** with 2.0 equiv of alkyllithium reagents resulted in a disproportionation to $[(Ph)_2nacnac]_2Cr$ (**2**) and CrR_4. **2** could be oxidized by treatment with tetrachloroethane to give trigonal-bipyramidal $[(Ph)_2nacnac]_2CrCl$ (**5**). Attempted alkylation of **5** with aluminum alkyls yielded the ortho-metalated product $(Ph)_2nacnac(\eta^1\text{-}C_6H_4\text{-}Ph)nacnacCr$ (**6**). However, the chromium(III) aryl complex $[(Ph)_2nacnac]_2CrPh$ (**4**) could be synthesized by reaction of $CrPh_3(THF)_3$ with 2 equiv of $(Ph)_2$nacnacH. Square-pyramidal **4** featured both a normal planar η^2-nacnac and a nonplanar η^3-nanac ligand. Thermolysis of **4** resulted in the loss of benzene along with the formation of **6**. The crystal structures of **2**, **3a**, and **4**−**6** were determined by X-ray diffraction. Complexes **1** and **3**−**5** catalyzed the polymerization of ethylene when activated with MAO, but they did not catalyze the polymerization by themselves.

Introduction

Beginning with work by Thomas et al.,[1,2] we have created a functional homogeneous model system of the so-called “Union Carbide catalyst” (Cp_2Cr/SiO_2)[3] for the polymerization of ethylene.[4,5] So faithful is this model that it reproduces one of the apparent disadvantages of the commercially used heterogeneous catalyst, namely its high selectivity for ethylene over propylene or, in other words, its sole utility for the production of high-density polyethylene (HDPE).[3] The stereoregular homopolymerization of propylene and the copolymerization of ethylene with α-olefins produce materials (i.e. PP, LLDPE) of considerable value, however. Such polymers can be made—inter alia—with the “Phillips catalyst” (inorganic Cr/SiO_2), one of the first polymerization catalysts to be discovered.[6] Despite several decades of investigation of this deceptively simple catalyst, there remain many open questions regarding the nature of the chromium sites responsible for initiation and propagation of polymerization.[7] In an attempt to build a homogeneous model system for the Phillips catalyst, we have turned to the “nacnac” ligands (i.e. N,N′-disubstituted β-diketiminates), which provide for coordination of chromium by two hard donor atoms and facilitate site isolation by steric protection with bulky substituents. The analogy between the presumed active site of the heterogeneous catalyst (**A**) and its homogeneous model (**B**) is depicted in Chart 1. The correspondence is obviously not perfect; nevertheless, some insight into the relevant chemistry of chromium might be expected to result from a study of “nacnac” chromium alkyls. Besides, any new chromium-based polymerization catalysts are of interest, and the compounds to be described fit into the larger context of our long-standing investigation of paramagnetic organometallics (i.e. “metallaradicals”).[8,9]

Chart 1

A **B**

Some time ago, we communicated preliminary experiments confirming the catalytic activity of $(Ph)_2$nacnac complexes of Ti(III), V(III), and Cr(III) ($(Ph)_2$nacnac = *N*,*N*′-diphenyl-2,4-pentanediimine anion).[10] Specifically, $(Ph)_2nacnacCrCl_2(THF)_2$/MAO catalyzed the copolymerization of ethylene with α-olefins. Seeking to avoid the ambiguities of MAO chemistry, we set out to explore the reactivity of well-defined $(Ph)_2$nacnacCr alkyls. Herein we report our findings with this particular ligand.

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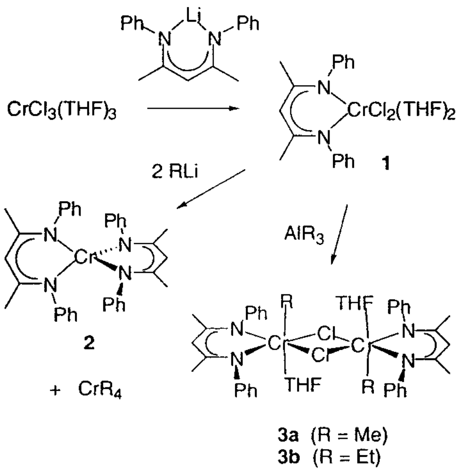
10.1021/om010857k CCC: $22.00

At the time of our first preparation of a nacnac chromium complex this class of bidentate monoanionic nitrogen analogues of the "acac" ligands had long been known but was effectively unexplored.[11−13] However, in the late 1990s the "nacnac" scent was apparently "in the air". Recent years have seen a flurry of activity in the area, and there are now numerous nacnac derivatives of early and late transition metals as well as representative elements.[14−63]

Scheme 1



Results and Discussion

As previously reported, slow addition of $[(Ph)_2$nacnac$]$-Li to a suspension of $CrCl_3(THF)_3$ in THF at room temperature yielded the six-coordinate dichloride complex $(Ph)_2$nacnac$CrCl_2(THF)_2$ (**1**; Scheme 1). The solid-state structure of **1** and its catalytic activity in the presence of methylaluminoxane (MAO) for the polymerization of ethylene and copolymerization of ethylene with α-olefins were described in an earlier communication.[10]

In an attempt to characterize more fully the catalytically active species in **1**/MAO mixtures, we set out to explore the organometallic chemistry of the $(Ph)_2$-nacnacCr moiety. However, alkylation of **1** proved less straightforward than the analogous vanadium chemistry, which easily yielded tetrahedral molecules of the type $(Ph)_2$nacnacVR_2. Thus, treatment of **1** with 2.0 equiv of lithium alkyls (e.g. Me_3SiCH_2Li or MeLi) in diethyl ether did not yield the desired dialkylchromium complexes but, rather, afforded dark green $[(Ph)_2$-nacnac$]_2Cr^{II}$ (**2**) in modest yield (see Scheme 1). The molecular structure of **2** has been determined by X-ray diffraction; it is depicted in Figure 1, and selected

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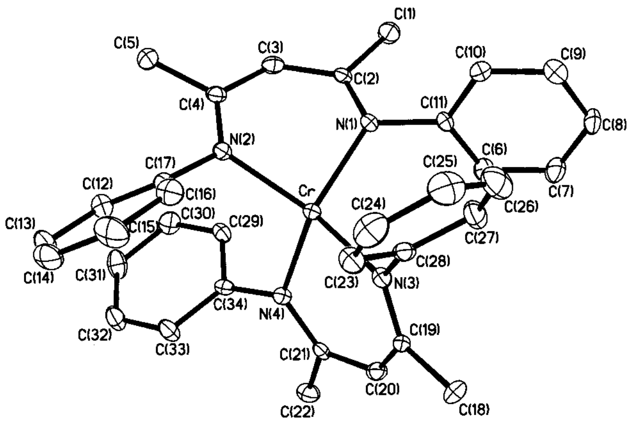

Figure 1. Molecular structure of $[(Ph)_2nacnac]_2Cr$ (**2**).

Table 1. Selected Interatomic Distances and Angles for $[(Ph)_2nacnac]_2Cr$ (2)

	Distances (Å)		
Cr−N(1)	2.058(3)	Cr−N(2)	2.049(4)
Cr−N(3)	2.055(4)	Cr−N(4)	2.069(3)
N(1)−C(2)	1.336(5)	N(1)−C(11)	1.451(5)
N(2)−C(4)	1.314(5)	N(2)−C(17)	1.432(5)
C(1)−C(2)	1.515(6)	C(2)−C(3)	1.401(6)
C(3)−C(4)	1.406(6)	C(4)−C(5)	1.513(6)
	Angles (deg)		
N(1)−Cr−N(2)	88.47(14)	N(1)−Cr−N(3)	105.49(14)
N(1)−Cr−N(4)	132.88(14)	N(2)−Cr−N(3)	149.78(14)
N(2)−Cr−N(4)	100.69(14)	N(3)−Cr−N(4)	89.35(14)
Cr−N(1)−C(2)	121.6(3)	Cr)−N(1)−C(11	119.2(3)
Cr−N(2)−C(40	126.2(3)	Cr−N(2)−C(17)	110.9(3)
Cr −N(3)−C(19)	125.5(3)	Cr−N(3)−C(28)	114.1(3)
Cr −N(4)−C(21)	123.1(3)	Cr−N(4)−C(34)	117.0(3)

interatomicdistances and angles are listed in Table 1. The molecule crystallized in the triclinic space group $P\bar{1}$ and featured no crystallographic symmetry. The coordination geometry of **2** deviates significantly from the square-planar coordination preferred by four-coordinate chromium(II).[64] Due presumably to the steric bulk of the phenyl substituents, **2** adopts the configuration of a distorted tetrahedron. Thus, the two nacnac planes (defined by N(1), N(2), C(2), C(3), C(4) and N(3), N(4), C(19), C(20), C(21)) are close to perpendicular at 80.3°. The average Cr−N distance in **2** (2.06 Å) is only marginally longer than that of **1** (2.033 Å), reflecting the opposing effects of lower coordination number and lower formal oxidation state. **2** is stable at ambient temperature in an inert atmosphere but decomposes quickly upon exposure to air. Its room-temperature effective magnetic moment is 5.1(1) μ_B, consistent with a chromium(II) compound containing four unpaired electrons.

While **2** might simply be considered a product of reduction of **1** by the electron-rich lithium alkyl followed by a nacnac-ligand transfer, the detection—by ^{1}H NMR spectroscopy—of the homoleptic chromium(IV) alkyl $Cr(CH_2SiMe_3)_4$[65,66] in the reaction mixture suggested that **2** was actually produced via disproportionation of the unstable target molecule $(Ph)_2nacnacCr(CH_2SiMe_3)_2$. The reaction of **1** with methyllithium also yielded **2**, along with unidentified side products (decomposition products of unstable $CrMe_4$?[67]). Tetrahedral coordination is neither common nor energetically advantageous for trivalent chromium (d^3). The coordination of two molecules of THF in **1** reflects the pronounced preference of Cr(III) for octahedral coordination. However, dialkyl derivatives are apparently not electrophilic enough to retain the THF ligands. Even the addition of stronger donors, such as pyridine, to the alkylation reactions failed to prevent the disproportionation.

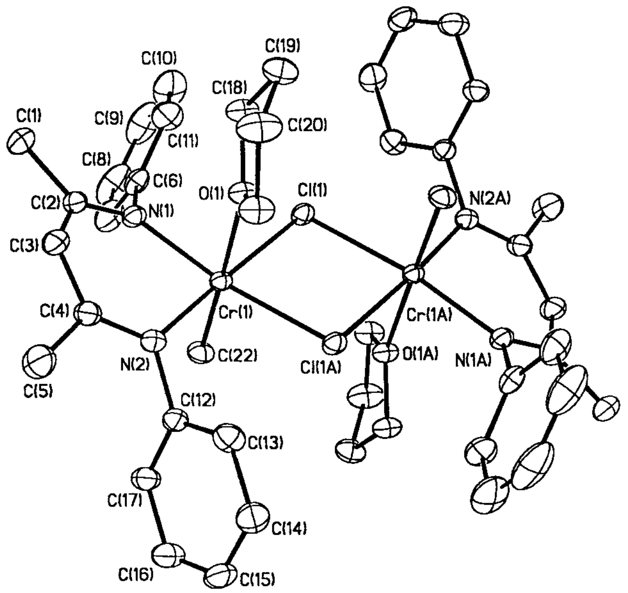

Figure 2. Molecular structure of $[(Ph)_2nacnacCr(CH_3)(\mu\text{-}Cl)THF]_2$ (**3a**).

In contrast, alkyls of the type $[(Ph)_2nacnacCr(THF)(R)(\mu\text{-}Cl)]_2$ (**3a**, R = Me; **3b**, R = Et) could be prepared by reaction of **1** with 1.0 equiv of the corresponding dialkyl zinc reagent (see Scheme 1). These molecules are closely related to $[(^iPr_2Ph)_2nacnacCr(Me)(\mu\text{-}Cl)]_2$, reported by Gibson et al.[19] **3a** is stable at room temperature in solution for an extended period of time, although it decomposes slowly upon exposure to air. Crystals of **3a** suitable for an X-ray structure determination were grown from a concentrated ether solution at −30 °C. Its molecular structure is shown in Figure 2, and selected interatomic distances and angles are listed in Table 2. The molecule lies on a crystallographic inversion center and adopts the geometry of an edge-sharing bioctahedron, emphasizing once again the preference of Cr(III) for octahedral coordination. The methyl groups are positioned trans to each other, and the Cr−Cl and Cr−C distances are within the expected ranges. The Cr−Cr distance of 3.63 Å does not allow for any direct metal−metal bonding; it is significantly longer than the corresponding distances in $[Cp^*Cr(\mu\text{-}Cl)CH_3]_2$ (3.29 Å)[68] and $[Cp^*Cr(\mu\text{-}Cl)(CH_2SiMe_3)]_2$ (3.47 Å).[69] The effective magnetic moment of **3** (5.4 μ_B; i.e. 3.8(1) μ_B per Cr) even shows that there is no magnetic coupling; it is the value expected for magnetically independent chromium(III) ions.

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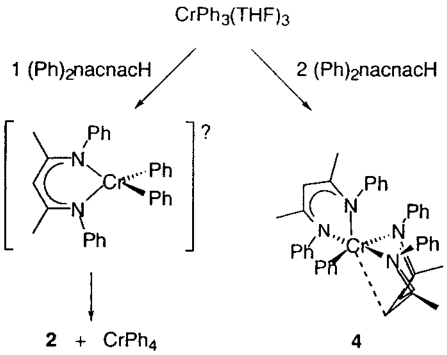
Table 2. Selected Interatomic Distances and Angles for [(Ph)$_2$nacnacCrMe(μ-Cl)THF]$_2$ (3)

Distances (Å)			
Cr(1)−N(1)	2.043(2)	Cr(1)−N(2)	2.058(2)
Cr(1)−C(22)	2.077(2)	Cr(1)−O(1)	2.269(2)
Cr(1)−Cl(1)	2.4127(6)	Cr(1)−Cl(1A)	2.4217(6)
N(1)−C(2)	1.334(3)	N(1)−C(6)	1.451(3)
N(2)−C(4)	1.327(3)	N(2)−C(12)	1.453(3)
C(1)−C(2)	1.523(3)	C(2)−C(3)	1.399(4)
C(3)−C(4)	1.418(3)	C(4)−C(5)	1.527(4)
Angles (deg)			
N(1)−Cr(1)−N(2)	91.07(8)	N(1)−Cr(1)−C(22)	93.21(9)
N(2)−Cr(1)−C(22)	92.25(9)	N(1)−Cr(1)−O(1)	85.59(7)
N(2)−Cr−(1)−O(1)	88.53(7)	C(22)−Cr(1)−O(1)	178.58(8)
N(1)−Cr(1)−Cl(1)	93.08(6)	N(1)−Cr(1)−Cl(1A)	171.57(6)
N(2)−Cr(1)−Cl(1A)	92.70(2)	N(2)−Cr(1)−Cl(1)	173.50(6)
C(22)−Cr(1)−Cl(1)	92.51(8)	C(22)−Cr(1)−Cl(1A)	94.17(7)
O(1)−Cr(1)−Cl(1)	86.80(5)	O(1)−Cr(1)−Cl(1A)	86.97(5)
Cl(1)−Cr(1)−Cl(1A)	82.54(2)	Cr(1)−Cl(1)−Cr(1A)	97.46(2)
Cr(1)−N(1)−C(2)	122.3(2)	Cr(1)−N(1)−C(6)	119.9(2)
Cr(1)−N(2)−C(12)	119.06(14)	Cr(1)−N(2)−C(4)	123.3(2)

Scheme 2



NMR spectroscopic observations suggested that **3a** adds THF reversibly. Thus, crystallization of the product of the reaction of **1** with $ZnMe_2$ from THF/Et_2O (rather than pure Et_2O) yielded a material that exhibited a ^1H NMR spectrum (in C_6D_6) different from **3a** but very similar to **1**. Trituration of this solid with diethyl ether restored the spectrum of **3a**. On the basis of these observations we assign the formula (Ph)$_2$nacnacCr(Me)(Cl)(THF)$_2$ to this compound. We also note that addition of excess pyridine to **3a** in C_6D_6 solution liberated THF and formed a new compound, tentatively identified as (Ph)$_2$nacnacCr(Me)(Cl)(py)$_2$.

As the targeted dialkyls were not readily accessible by alkylation of the dichloride **1**, we sought another preparatory route to such compounds. While many chromium alkyls of the type $CrR_3(THF)_3$ are thermally labile (especially if R is small), $CrPh_3(THF)_3$ proved a suitable precursor. Addition of 1 equiv of (Ph)$_2$nacnacH to a stirred solution of $CrPh_3(THF)_3$ in THF caused a color change from red to dark green; however, standard workup yielded the bis-nacnac compound **2** again. This result is consistent with our earlier inference that compounds of the type (Ph)$_2$nacnacCrR$_2$ decompose via disproportionation. In this particular instance, formation of (Ph)$_2$nacnacCr(Ph)$_2$ is presumably followed by rapid disproportionation to **2** and Cr(Ph)$_4$ (not identified) (Scheme 2).

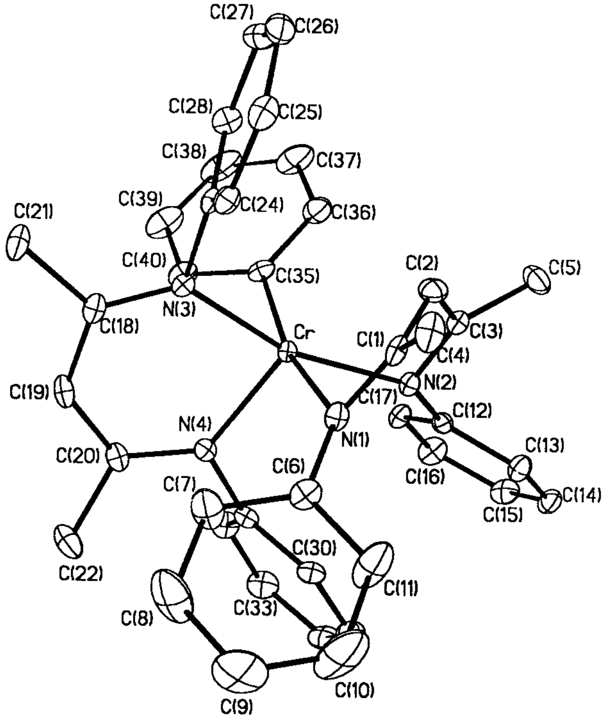


Figure 3. Molecular structure of [(Ph)$_2$nacnac]$_2$CrPh (**4**).

Table 3. Selected Interatomic Distances and Angles for [(Ph)$_2$nacnac]$_2$CrPh (4)

Distances (Å)			
Cr−N(1)	2.114(3)	Cr−N(2)	2.060(3)
Cr−N(3)	2.043(2)	Cr−N(4)	2.004(3)
Cr−C(35)	2.086(3)	N(1)−C(1)	1.306(4)
N(1)−C(6)	1.422(4)	N(2)−C(3)	1.316(4)
N(2)−C(12)	1.427(4)	C(1)−C(2)	1.433(5)
C(1)−C(4)	1.518(4)	C(2)−C(3)	1.424(4)
C(3)−C(5)	1.511(5)		
Angles (deg)			
N(1)−Cr−N(2)	84.37 (10)	N(1)−Cr−N(3)	91.14(10)
N(1)−Cr−N(4)	95.06 (10)	N(1)−Cr−C(35)	167.23(12)
N(2)−Cr−N(3)	161.98 (11)	N(2)−Cr−N(4)	106.84(11)
N(2)−Cr−C(35)	92.02 (11)	N(3)−Cr−N(4)	90.91(11)
N(3)−Cr−C(35)	88.55 (11)	N(4)−Cr−C(35)	97.71(12)

In an attempt to avoid the disproportionation of the chromium(III) alkyls/aryls, we next investigated the possibility of stabilizing an organochromium(III) compound by coordinating two nacnac ligands to the metal center. Addition of 2 equiv of (Ph)$_2$nacnacH to a stirred solution of $CrPh_3(THF)_3$ in THF produced a slight color change from red to brown-red. Subsequent workup of the reaction mixture yielded red crystals of [(Ph)$_2$nacnac]$_2$CrPh (**4**) in good yield (72%) (see Scheme 2). The room-temperature magnetic moment of 4.1(1) μ_B is consistent with the molecule being a mononuclear chromium(III) species. The crystal structure of **4** was determined by X-ray diffraction, and the result is shown in Figure 3. Selected interatomic distances and angles are listed in Table 3.

4 belongs to the relatively small number of five-coordinate Cr(III) complexes.[69−74] The coordination geometry of chromium is best described as a slightly distorted square pyramid with N(4) occupying the apical

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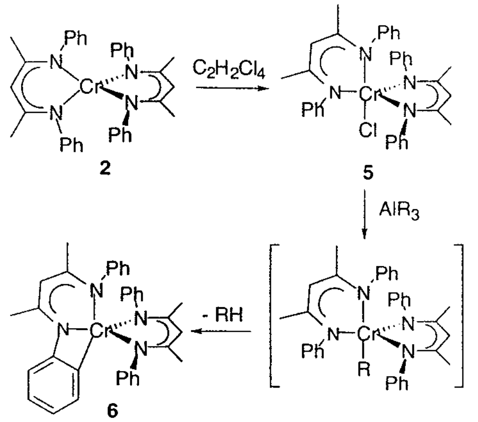
Scheme 3



site. This leaves an open coordination site trans to N(4). The latter is probably responsible for the most remarkable structural feature of **4**, namely the nonplanarity of the nacnac ligand containing N(1) and N(2). This CrN_2C_3 ring adopts a boat configuration that brings C(2) in relatively close contact to the metal (Cr−C(2) = 2.56 Å). The relevant dihedral angles are 106.8° between the Cr, N(1), N(2) plane and the N(1), N(2), C(1), C(3) plane and 146.2° between the latter and the C(1), C(2), C(3) plane. There are no short intermolecular contacts to C(2). Following an argument presented by Piers et al.,[48] based on calculations by Tolman and Solomon et al.,[43] we suggest that the bonding of this nacnac ligand should not be described as η^5-coordination but, rather, results from an interaction of chromium with the highest occupied π-orbital of the nacnac ligand, which has significant electron density on C(2) and none on C(1) and C(3). In effect, the nacnac ligand becomes a tridentate σ-donor coordinating to the metal via N(1), N(2), and C(2). The Cr−N(1) distance of 2.114 Å is longer than the other Cr−N distances in the molecule, due to the trans influence of the phenyl ligand.

With the intent of creating a starting material for alkyls of the type $[(Ph)_2nacnac]_2CrR$, we set out to explore the oxidation of **2**. A more straightforward synthesis of **2** involves reaction of $CrCl_2$ with 2 equiv of $(Ph)_2nacnacLi$ in diethyl ether. Solutions of **2** were easily oxidized by stirring for 12 h with $^1/_2$ equiv of 1,1,2,2-tetrachloroethane, which results in a gradual color change from dark green to brown-red. Slow evaporation of a diethyl ether solution of the compound deposited large crystals of $[(Ph)_2nacnac]_2CrCl$ (**5**, Scheme 3) in 73% yield. The molecular structure of **5** was determined by X-ray diffraction; it is shown in Figure 4, and selected interatomic distances and angles are listed in Table 4. Complex **5** is a mononuclear trigonal-bipyramidal complex with the chloride atom occupying an axial site. Like **4**, **5** is an example of a 5-coordinate chromium(III) complex.[69−74] However, unlike compound **4**, the molecule possesses two planar nacnac ligands bonded in a bidentate fashion. The Cr−Cl distance of 2.33 Å is within the expected range and is comparable to those found in **1** (Cr−Cl, 2.346 Å).[10] Although the solid-state structure of **5** features two inequivalent nacnac ligands, the ^1H NMR spectrum of **5** is very simple. Apparently, in solution at room temperature compound **5** is fluxional, rendering the ligands equivalent on the ^1H NMR time scale.

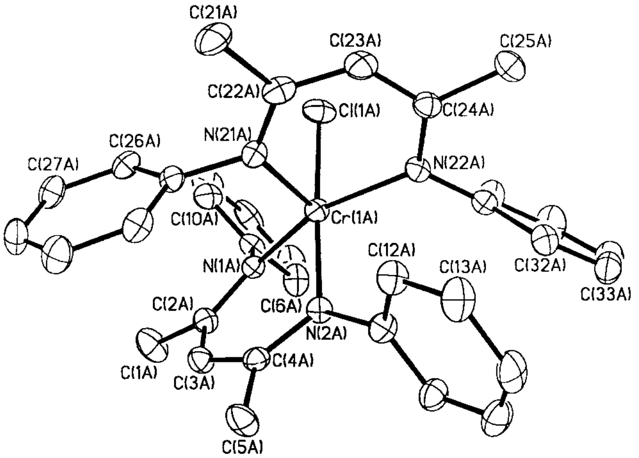


Figure 4. Molecular structure of one of the two independent molecules of $[(Ph)_2nacnac]_2CrCl$ (**5**).

Table 4. Selected Interatomic Distances and Angles for One of the Two Independent Molecules of $[(Ph)_2nacnac]_2CrCl$ (5)

	Distances (Å)		
Cr(1)−N(21)	1.970(4)	Cr(1)−N(22)	2.021(4)
Cr(1)−N(2)	2.032(4)	Cr(1)−N(1)	2.068(4)
Cr(1)−Cl(1)	2.327(2)		
	Angles (deg)		
N(21)−Cr(1)−N(22)	90.3 (2)	N(21)−Cr(1)−N(2)	90.9(2)
N(22)−Cr(1)−N(2)	92.8 (2)	N(21)−Cr(1)−N(1)	114.0(2)
N(22)−Cr(1)−N(1)	155.7 (2)	N(2)−Cr(1)−N(1)	88.1(2)
N(21)−Cr(1)−Cl(1)	94.17 (13)	N(22)−Cr(1)−Cl(1)	87.62(12)
N(2)−Cr(1)−Cl(1)	174.95 (11)	C(2)−N(1)−Cr(1)	122.8(3)
C(11)−N(1)−Cr(1)	122.8 (3)	C(17)−N(2)−Cr(1)	122.3(3)
C(4)−N(2)−Cr(1)	121.8 (3)	C(22)−N(21)−Cr(1)	126.7(3)
C(31)−N(21)−Cr(1)	113.5 (3)	C(37)−N(22)−Cr(1)	114.9(3)
C(24)−N(22)−Cr(1)	125.8 (3)		

Strongly reducing alkylating reagents such as RLi and RMgCl reduce the chloride complex **5** right back to **4**. Therefore, less electron rich aluminum alkyls were employed. Addition of 1 equiv of $AlMe_3$ to a stirred solution of **5** resulted in an immediate color change to dark red. Workup of the reaction mixture with pentane or diethyl ether gave a new paramagnetic compound (**6**), as indicated by ^1H NMR spectroscopy. The compound was initially assigned the formula $[(Ph)_2nacnac]_2CrMe$, and in accord with that supposition it reacted with hydrogen chloride to regenerate the starting material **5**. However, several observations militated against this assignment. Most importantly, reaction of **5** with $AlEt_3$ produced the identical compound **6**, as judged by its ^1H NMR spectrum. Also surprising was the fact that compound **6** did not polymerize ethylene, even in the presence of MAO. Finally, when the reactions of **5** with aluminum alkyls AlR_3 were monitored by ^1H NMR spectroscopy, resonances for methane (R = Me) or ethane (R = Et) appeared along with those of **6**.

Ultimately, the determination of the molecular structure of **6** by X-ray diffraction solved the puzzle. The result is depicted in Figure 5, and selected interatomic distances and angles of **6** are listed in Table 5. The molecule is a five-coordinate chromium(III) aryl, with the aryl group also being one of the N-substituents of a nacnac moiety. In other words, **6** is the product of an ortho metalation of the intermediate $[(Ph)_2nacnac]_2CrR$ to generate RH and **6** (Scheme 3). The room-temperature magnetic moment of 3.6(1) μ_B is consistent with

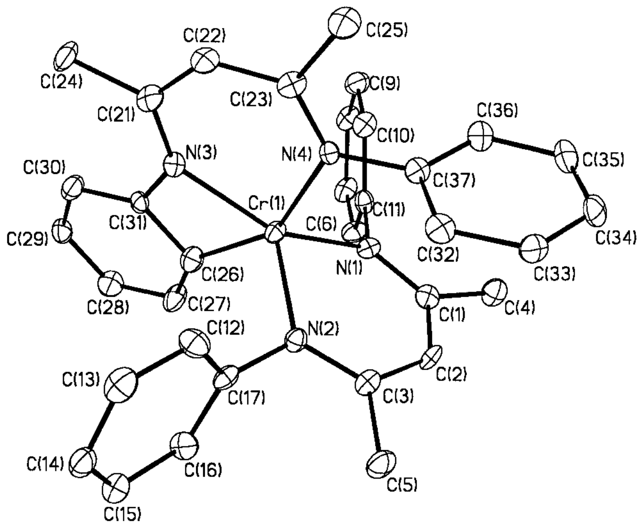


Figure 5. Molecular structure of (Ph)$_2$nacnac(η^1-C_6H_4-Ph)nacnacCr (**6**).

Table 5. Selected Interatomic Distances and Angles for (Ph)$_2$nacnac(η^1-C_6H_4-Ph)nacnacCr (6)

	Distances (Å)		
Cr(1)−N(1)	1.976(5)	Cr(1)−N(2)	1.979(5)
Cr(1)−N(3)	2.005(5)	Cr(1)−N(4)	2.099(5)
Cr(1)−C(26)	2.062(7)	N(4)−C(23)	1.336(9)
N(4)−C(37)	1.443(8)	N(3)−C(21)	1.339(8)
N(3)−C(31)	1.396(8)	C(26)−C(31)	1.392(10)
C(21)−C(24)	1.519(9)	C(21)−C(22)	1.401(10)
C(23)−C(25)	1.511(10)	C(22)−C(23)	1.403(10)
	Angles (deg)		
N(1)−Cr(1)−N(2)	89.7(2)	N(1)−Cr(1)−N(3)	142.8(2)
N(1)−Cr(1)−N(4)	126.0(2)	N(1)−Cr(1)−C(26)	99.6(3)
N(2)−Cr(1)−N(3)	97.9(2)	N(2)−Cr(1)−N(4)	98.5(2)
N(2)−Cr(1)−C(26)	102.0(3)	N(3)−Cr(1)−N(4)	87.5(2)
N(3)−Cr(1)−C(26)	66.2(3)	N(4)Cr(1)−C(26)	153.0(3)
Cr(1)−N(3)−C(31)	95.2(4)	N(3)−C(31)−C(26)	105.6(6)
Cr(1)−C(26)−C(31)	92.9(5)		

the molecule being a mononuclear chromium(III) complex. The Cr−C distance of 2.06 Å lies within the range found for organochromium(III) compounds. The structure of **6** also explains its reactivity toward HCl and ethylene, as noted above.

Given the apparent propensity of alkyls of the type [(Ph)nacnac]$_2$CrR to suffer ortho metalation, we investigated the thermal stability of phenyl derivative **4**. Interestingly, compound **4** is stable for days at room temperature in solution, with no apparent formation of **6** observed in the ^{1}H NMR spectrum. However, heating **4** to 70 °C for several days cleanly generated **6** and benzene. The enhanced kinetic stability of **4** relative to the alkyl derivatives may well be a ground-state effect, reflecting its greater chromium−carbon bond strength.

Polymerization Experiments. Our previous work in Cp*Cr chemistry has shown that coordinatively unsaturated chromium(III) alkyls are catalysts for the polymerization of ethylene.[5] Accordingly, a solution of **3a** showed no tendency to react with ethylene, since it is coordinatively saturated. When activated with MAO, the dinuclear alkyl **3a** catalyzed the polymerization of ethylene (as did **1**). It did not react with propylene or 1-hexene, even when activated with MAO, nor did it catalyze the copolymerization of 1-hexene or propylene with ethylene. The results of the polymerization experiments are listed in Table 6.

Table 6. Results of Polymerization Experiments[a]

catalyst	[Cr], μM	monomer	yield, g	M_w	M_n	M_w/M_n
1, MAO	77.6	C_2H_4	10.5	1 157 039	15 892	72.8
1, MAO	77.6	C_2H_4/propylene	0.3	209 900	2 050	53.9
1, MAO	77.6	C_2H_4/1-hexene	8.7	9 659	1 402	6.9
3a, MAO	21.2	C_2H_4	7.8	1 629 000	9 500	171.5
3a, MAO	21.2	C_2H_4/1-hexene	13.2	22 816	4 316	5.3
4, MAO	12.0	C_2H_4	0.7	298 000	15 500	19.2
5, MAO	12.0	C_2H_4	18.0	350 052	7 071	49.5
5, MAO	12.0	C_2H_4/1-hexene	1.6	916 214	28 365	32.3

[a] See the Experimental Section for details.

5/MAO was a very productive catalyst for the polymerization of ethylene. This observation raised questions about the nature of the active species. One accepted function of MAO (which always contains some $AlMe_3$) is that of an alkylating agent, which should transform **5** into [(Ph)$_2$nacnac]$_2$CrMe. However, we have shown this compound to be unstable, decomposing to **6** (see Scheme 3), which is catalytically inactive. What role MAO plays in possibly suppressing the ortho-metalation reaction of [(Ph)$_2$nacnac]$_2$CrMe and in its activation remains unclear. While complete abstraction of the sole alkyl group would seem to render an ethylene insertion impossible, we note that polarization of a metal alkyl by a Lewis acid has been proposed to enhance polymerization activity.[75] An attempted copolymerization of ethylene with 1-hexene using **5**/MAO yielded merely polyethylene without significant incorporation of comonomer.

Although we could not test the catalytic activity of bis-nacnac chromium alkyls due to their instability, we have tried the analogous chromium aryl compound **4**. While it is coordinatively unsaturated, it did not react with ethylene by itself. Even in the presence of MAO the catalytic activity of **4** was relatively low, yielding only a small amount of polymer.

We note that the polymers produced in these experiments featured very broad and multimodal molecular weight distributions (M_w/M_n) not at all characteristic of homogeneous single-site catalysts. We do not care to speculate on the various active species generated in these MAO-containing solutions; however, nacnac ligand transfer from chromium to aluminum must be considered a possibility. Rather, we shall continue our search for well-defined catalysts that do not require activation by cocatalysts.

Conclusions

We have prepared and structurally characterized several organometallic derivatives of the (Ph)$_2$nacnacCr^{III} fragment. None of these molecules catalyze the polymerization of ethylene by themselves; however, activation by MAO transformed most of them into active catalysts. The scope of the organometallic chemistry of chromium with this particular nacnac ligand is limited by tendencies to disproportionate and suffer ortho metalation. These obstacles can be overcome by judicious substitution of the N-aryl groups. The results of this approach will be the subject of future publications.

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Experimental Section

General Considerations. All manipulations of compounds were carried out using standard Schlenk, vacuum, and glovebox techniques. Pentane, diethyl ether, tetrahydrofuran, and toluene were distilled from purple Na benzophenone/ketyl solutions. C_6D_6 and CD_2Cl_2 were predried with sodium and stored under vacuum over 4 Å molecular sieves. $CrCl_3$ (anhydrous) was purchased from Strem Chemical Co. ((Trimethylsilyl)methyl)lithium was purchased as a 1 M solution in pentane, was crystallized from solution at −30 °C, and was isolated as a white crystalline solid. Methyllithium, diethylzinc, and dimethylzinc were purchased from Aldrich and were used as received. $CrCl_3(THF)_3$ and $CrPh_3(THF)_3$ were prepared according to literature procedures.[76,77]

NMR spectra were taken on a Bruker AM-250 spectrometer and were referenced to the residual protons of the solvent (C_6D_6, 7.15 ppm; CD_2Cl_2, 5.32 ppm). FTIR spectra were taken on a Mattson Alpha Centauri spectrometer with a resolution of 4 cm^{-1}. UV/vis spectra were taken using a Bruins Instruments Omega 20 spectrophotometer. Mass spectra were obtained by the University of Delaware Mass Spectrometry Facility. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

Room-temperature magnetic susceptibilities were determined using a Johnson Matthey magnetic susceptibility balance.

Preparation of (*N*,*N*′-Diphenyl-2,4-pentanediiminato)dichlorochromium(III) Bis(tetrahydrofuran), $(Ph)_2$nacnac$CrCl_2(THF)_2$ (1). $(Ph)_2$nacnacH (0.6 g, 2.40 mmols) was dissolved in 50 mL of THF and cooled to −30 °C. Methyllithium (2.40 mmols, 53 mg) was slowly added as a solid with stirring. The THF solution of $(Ph)_2$nacnacLi prepared in situ was then slowly added over 3 h to a slurry of $CrCl_3(THF)_3$ (900 mg, 2.40 mmols) in 150 mL of THF. The color of the solution changed from purple to red-brown. After it was stirred overnight at room temperature, the reaction mixture was concentrated to 50 mL and cooled to −30 °C for crystallization. A brown microcrystalline powder was isolated by filtration. After the powder was washed several times with cold THF and dried under vacuum, 1.08 g (2.09 mmol, 87%) of **1** was isolated. ^{1}H NMR (THF-d_8; δ): 15.5 (6H), 6.2 (4H) ppm. IR (KBr; cm^{-1}): 3050 (w), 3017 (m), 2966 (s), 2928 (s), 2883 (s), 1590 (w), 1555 (vs), 1530 (vs), 1484 (vs), 1448 (vs), 1387 (vs), 1263 (s), 1200 (s), 1065 (w), 1017 (s), 921 (m), 871 (s), 848 (s), 764 (m), 710 (s), 662 (w), 526 (m), 477 (w). Anal. Calcd. for $C_{25}H_{33}N_2O_2CrCl_2$: C, 58.14; H, 6.44; N, 5.42. Found: C, 57.95; H, 6.81; N, 5.51.[78] MS (*m*/*z* (%)): 370.76 (41.24) [$M^+ - 2THF$], 335.81 (41.60) [$M^+ -$ Cl, 2THF], 300.86 (6.01) [$M^+ -$ 2Cl, 2THF]. UV/vis (Et_2O; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 527 (572), 419 (8233), 400 (5712). μ_{eff}(294 K) = 4.1(1) μ_B. Mp: 174−180 °C dec.

Reaction of (*N*,*N*′-Diphenyl-2,4-pentanediiminato)dichlorochromium(III) Bis(tetrahydrofuran) (1) with MeLi. **1** (0.600 g, 1.16 mmol) was dissolved in THF and cooled to −30 °C. Two equivalents of MeLi (1.66 mL, 1.4 M solution in diethyl ether) was added dropwise to the solution of **1**. The reaction mixture rapidly turned brown. After the mixture was stirred at room temperature for 4 h, it was evaporated to dryness. THF was removed by trituration with ether. The resulting solid was extracted with ether and filtered to remove LiCl. The black-green filtrate was then concentrated and cooled to −30 °C for crystallization. Dark green crystals of $[(Ph)_2$nacnac$]_2$Cr (**2**; 210 mg, 35%) were isolated. ^{1}H NMR (C_6D_6; δ): 124.0 (6H, vb), 7.6 (4H), 4.4 (6H), −16.8 (1H, vb) ppm. IR (KBr; cm^{-1}): 3055 (w), 3029 (w), 2922 (w), 2879 (m), 1591 (w), 1540 (s), 1515 (m), 1482 (s), 1449 (m), 1382 (vs), 1276 (w), 1264 (w), 1021 (m), 866 (w), 842 (w), 752 (w), 700 (m). Anal. Calcd for $C_{34}H_{34}N_4Cr$: C, 74.16; H, 6.22; N, 10.17. Found: C, 72.42; H, 6.30; N, 10.01.[78] MS (*m*/*z* (%)): 550.22 (100) [M^+], 301.05 (45.75) [$M^+ - C_{17}H_{17}N_2$]. UV−vis (Et_2O; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 348 (sh) (10 445). μ_{eff}(294 K) = 5.1(1) μ_B. Mp: 220 °C dec.

Independent Synthesis of Bis(*N*,*N*′-diphenyl-2,4-pentanediiminato)chromium(II), $[(Ph)_2$nacnac$]_2$Cr (2). $(Ph)_2$nacnacH (4.0 g, 16 mmol) was dissolved in 50 mL of THF and cooled to −30 °C. MeLi (0.352 g, 16 mmol) was added to the THF solution of $(Ph)_2$nacnacH. The resulting THF solution of $(Ph)_2$nacnacLi was then added dropwise to the suspension of $CrCl_2$ (0.983 g, 8.0 mmol) in 150 mL of THF over 1 h from an addition funnel. The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with diethyl ether. The extract was then filtered to remove LiCl and concentrated for crystallization. Dark crystals of $[(Ph)_2$nacnac$]_2$Cr (**2**; 3.7 g, 7.09 mmol, 84% yield) were isolated from a concentrated diethyl ether solution cooled to −30 °C.

Preparation of Bis(*N*,*N*′-diphenyl-2,4-pentanediiminato)dichlorodimethyldichromium(III) Bis(tetrahydrofuran) (3a). To a stirred solution of (Ph)nacnac$CrCl_2(THF)_2$ (0.800 g, 1.5 mmol) in 40 mL of THF was added 0.852 mL of dimethylzinc (2.0 M solution in toluene, 1.7 mmol). Stirring for 10 min followed by removal of solvent gave a dark brown-green solid. Crystallization from a concentrated diethyl ether solution at −30 °C yielded 0.556 g (84%) of **3** as dark brown crystals. ^{1}H NMR (CD_2Cl_2; δ): 77.8 (vb, 6H), 12.5 (vb, 4H), 9.2 (b, 4H), 7.1 (b, 4H), 2.4 (b, 4H), −4.3 (b, 2H) ppm. IR (KBr; cm^{-1}): 3055 (w), 2972 (m), 2902 (m), 1572 (s), 1526 (m), 1485 (s), 1459 (vs), 1424 (s), 1257 (w), 1197 (m), 1171 (w), 1070 (w), 1014 (m), 927 (w), 865 (s), 845 (s), 755 (m), 706 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{56}N_4O_2Cl_2Cr_2$: C, 62.33; H, 6.66; N, 6.61. Found: C, 59.05; H, 6.61; N, 6.21.[78] MS (*m*/*z* (%)): 350 (23) [$M^+ -$ THF], 301 (1.44) [$M^+ -$ THF, Cl, Me]. UV/vis (Et_2O; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 499 (413). μ_{eff}(294 K) = 3.8(1) μ_B. Mp: 190 °C.

Preparation of Bis(*N*,*N*′-diphenyl-2,4-pentanediiminato)dichlorodiethyldichromium(III) Bis(tetrahydrofuran) (3b). To a stirred solution of (Ph)nacnac$CrCl_2(THF)_2$ (0.800 g, 1.5 mmol) in 50 mL of THF was added 0.185 g of diethylzinc (1.5 mmol). Stirring for 10 min, followed by removal of solvent, gave a dark brown-green solid. Crystallization from a concentrated diethyl ether solution at −30 °C yielded 0.520 g (76%) of **3b** as dark brown crystals. ^{1}H NMR (C_6D_6; δ): 90.5 (6H), 13.4 (4H), 9.1 (4H), 6.9 (4H), 2.7 (4H), −10.9 (3H) ppm. IR (KBr; cm^{-1}): 3055 (w), 3017 (w), 2958 (m), 2928 (m), 2895 (m), 2839 (m), 1593 (w), 1539 (s), 1484 (s), 1449 (s), 1383 (s), 1261 (s), 1190 (s), 1117 (w), 1069 (w), 1024 (m), 893 (w), 842 (m), 755 (m), 700 (s). Anal. Calcd for $C_{46}H_{60}N_4O_2Cl_2Cr_2$: C, 63.08; H, 6.90; N, 6.40. Found: C, 58.40; H, 6.54; N, 5.49.[78] MS (*m*/*z* (%)): 250 (100) [−THF, Et and Cl]; 803 (0.16) [−THF]. UV/vis (Et_2O; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 534 (534). μ_{eff}(294 K) = 3.7 (1) μ_B. Mp: 103−105 °C.

Preparation of Bis(*N*,*N*′-diphenyl-2,4-pentanediiminato)phenylchromium(III) (4). $CrPh_3(THF)_3$ (0.400 g, 0.8 mmol) was dissolved in 50 mL of THF and 2.0 equiv of $(Ph)_2$nacnacH (0.400 g, 1.6 mmol) was added. The solution was stirred for 1 h, during which time its color changed from light red to brown-green. All volatiles were removed, and the resulting solid was dissolved in pentane to give a dark red solution. The pentane solution was concentrated and cooled to −30 °C for crystallization. Dark red crystals of **4** were isolated in 72% yield (0.362 g). ^{1}H NMR (C_6D_6; δ): 36 (vb, 6H), 8.4 (12H), 5.0 (12H) ppm. IR (KBr; cm^{-1}): 3052 (m), 2996 (w), 2959 (w), 2922 (w), 1593 (m), 1549 (s), 1523 (s), 1485 (s), 1452

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(78) Several of the compounds reported here have yielded low values for carbon in their elemental analyses. This deficiency could not be remedied by several crystallizations and repeated analyses. While we are convinced of the purity of the samples submitted for analysis, we have no explanation for the discrepancies.

Table 7. Crystallographic Data for 2, 3a, and 4−6

	2	**3a**	**4**	**5**	**6**
formula	$C_{34}H_{34}Cr$	$C_{44}H_{56}Cl_2Cr_2N_4O_2$	$C_{40}H_{39}CrN_4$	$C_{34}H_{34}ClCrN_4$	$C_{34}H_{33}CrN_4$
fw	550.65	847.83	627.75	586.10	549.64
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
color	dark green	red	dark brown	brown	red
a, Å	10.54650(10)	12.1282(3)	9.6543(2)	9.23610(2)	10.0898(3)
b, Å	11.4442(2)	14.2684(3)	17.6528(2)	17.7197(2)	9.2347(3)
c, Å	13.8021(2)	12.8048(3)	20.0308(3)	19.1786(3)	30.2026(5)
α, deg	87.5203(9)	90	90	73.9512(6)	90
β, deg	72.7442(8)	90.3352(4)	101.7650(9)	83.5156(2)	97.814(2)
γ, deg	65.3308(3)	90	90	82.8597(6)	90
V, Å^3	1439.44(5)	2215.83(4)	3342.01(4)	2982.86(5)	2788.03(13)
Z	2	2	4	4	4
D(calcd), g cm^{-3}	1.270	1.271	1.248	1.305	1.309
μ(Mo Kα), cm^{-1}	4.27	6.50	3.76	5.03	4.40
temp, K	218(2)	213(2)	173(2)	198(2)	173(2)
no. of data/params	8660/352	4805/244	5099/407	11123/721	4280/352
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)				
GOF on F^2	1.143	1.036	1.088	1.004	1.770
$R(F)$, %	8.87[a]	4.49[a]	5.42[a]	7.13[a]	9.55[a]
$R_w(F^2)$, %	21.76[a]	13.26[a]	14.40[a]	17.49[a]	25.78[a]

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

(s), 1401 (vs), 1266 (m), 1189 (m), 1070 (w), 1025 (m), 920 (w), 843 (w), 751 (m), 698 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{39}N_4Cr$: C, 76.53; H, 6.26; N, 8.92. Found: C, 75.82; H, 6.12; N, 8.71.[78] MS (m/z (%)): 627.3 (6) [M$^+$], 550.23 (21) [M$^+$ − C_6H_5]. UV/vis (Et_2O; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 547 (487), 660 (156). μ_{eff} (294 K): 4.1(1) μ_B. Mp: 145−147 °C.

Bis(*N*,*N*′-diphenyl-2,4-pentanediiminato)chlorochromium(III), [(Ph)$_2$nacnac]$_2$CrCl (5). [(Ph)$_2$nacnac]$_2$Cr (0.8 g, 1.45 mmol) was dissolved in 100 mL of diethyl ether. Addition of tetrachloroethane (0.076 mL, 0.726 mmol) to the diethyl ether solution with stirring caused no immediate color change. After the mixture was stirred overnight, a brown-red solution was obtained. Evaporation of solvent yielded a dark brown solid that was extracted with diethyl ether. Brown needles (0.620 g, 73% yield) were isolated by slow evaporation of solvent at room temperature. ^1H NMR (C_6D_6): 38.5 (12H, vb), 7.1 (20H, b) ppm. IR (KBr; cm^{-1}): 3054 (s), 3017 (m), 2962 (w), 2920 (m), 1592 (m), 1528 (s), 1497 (s), 1410 (s), 1388 (s), 1254 (m), 1185 (m), 1070 (w), 1024 (m), 940 (w), 916 (w), 841 (w), 754 (m), 705 (s), 518 (w) cm^{-1}. Anal. Calcd for $C_{34}H_{34}N_4ClCr$: C, 69.7; H, 5.8; N, 9.56. Found: C, 69.41; H, 6.03; N, 9.67. MS (m/z (%)): 585.13 (78.3) [M$^+$], 550.1522 (100) [M$^+$ − Cl]. UV/vis (diethyl ether; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 656.0 (316), 663.0 (304), 766 (178). μ_{eff} (294 K): 4.1(1) μ_B. Mp: 150−152 °C.

Reaction of 5 with Trimethylaluminum. Isolation of (Ph)$_2$nacnac(η^1-C_6H_4-Ph)nacnacCr (6). **5** (300 mg, 0.53 mmol) was dissolved in 35 mL of diethyl ether. Slow addition of 0.039 g of trimethylaluminum caused an immediate color change from dark brown-red to dark red. After the mixture was stirred for 10 min, the volatiles were removed. Dark red crystals of **6** were isolated in 71% yield (200 mg) from a concentrated pentane solution at −30 °C. ^1H NMR (C_6D_6; δ): 91 (vb, 6H), 50.2 (3H), 44.6 (3H), 17.1 (2H), 13.9 (4H), 7.2 (2H), 5.1 (4H), −1.5 (3H), −6.5 (4H), −11.1 (2H) ppm. IR (KBr; cm^{-1}): 3056 (w), 3010 (w), 2982 (w), 2923 (w), 1592 (m), 1551 (s), 1522 (s), 1482 (s), 1451 (s), 1391 (s), 1263 (m), 1191 (m), 1069 (w), 1025 (m), 915 (w), 832 (w), 754 (m), 701 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{33}N_4Cr$: C, 74.36; H, 6.06; N, 10.20. Found: C, 74.54; H, 6.42; N, 9.94. MS (m/z (%)): 550 (9.29) [M$^+$], 301 (2.3) [M$^+$ − (Ph)$_2$nacnac]. UV/vis (Et_2O): λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 853 (203), 672 (112). μ_{eff} (294 K) = 3.6(1) μ_B. Mp: 130 °C.

Crystallographic Structure Determinations. Crystal, data collection, and refinement parameters are given in Table 7. Suitable crystals for data collection were selected and mounted with epoxy cement on the tip of a fine glass fiber or in nitrogen-flushed, thin-walled glass capillaries. All data were collected at 173 K with a Siemens P4/CCD diffractometer with graphite-monochromated Mo Kα X-radiation ($\lambda = 0.710\ 73$ Å). All specimens of **2** and **6** showed diffuse diffraction characterized by broad line widths, which affected resolution and led to fairly high R factors. No symmetry higher than triclinic was observed in the diffraction data of **2** and **5**. E statistics suggested the centrosymmetric space group $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The diffraction data of **3a**, **4**, and **6** were uniquely consistent with the reported monoclinic space groups. Structure **3a** resides on a crystallographic inversion center. There are two chemically equivalent, but crystallographically independent, molecules in the asymmetric unit of **5**. Structures **3a**, **4**, **5**, and **6** were solved by direct methods and structure **2** by way of the Patterson function. All structures were completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogens were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

General Ethylene Polymerization Procedure. In a glovebox, the precatalyst (0.012−0.21 mmol) was dissolved in 50 mL of CH_2Cl_2. To the precatalyst was added MAO (10 wt % solution in toluene, Al/Cr = 100); the mixture was placed in a sealed Parr reactor, and the apparatus was removed from the glovebox. The reactor was charged with ethylene at 300 psi and kept at a constant pressure. After 1 h the ethylene supply was closed and the reaction vessel was vented. The resulting polymer was washed with a methanol/7 M aqueous HCl (1:1) mixture followed by deionized water. The polymer was dried under vacuum at 60 °C for 18 h.

General Ethylene/Hexene Copolymerization Procedure. Inside the glovebox the precatalyst was dissolved in 25 mL of CH_2Cl_2, and MAO (10 wt. % solution in toluene, Al/Cr = 100) was added to the solution. A 23.0 g amount of dried 1-hexene was added to the reaction mixture, and the contents were placed in a Parr reactor and removed from the glovebox. Ethylene (300 psi) was charged into the reactor. After 1 h of stirring the ethylene supply was closed and the reactor vented. The polymer was washed and dried as for the polyethylene (see above).

General Ethylene/Propylene Polymerization Procedure. Inside the glovebox the precatalyst was dissolved in 50 mL of CH_2Cl_2. To this solution was added MAO (Al/Cr = 100). The reaction mixture was placed in a Parr reactor and removed from the glovebox. The reactor was first charged with propylene (100 psi) for approximately 5 min, and then the propylene supply was shut off. Ethylene (350 psi) was then charged into the reactor for 1 h. The resulting polymer was handled as above.

Acknowledgment. This research was supported by grants from the National Science Foundation (Grant No. CHE-9876426) and Chevron Chemical Co. (now Chevron Phillips Chemical Co. LP).

Supporting Information Available: Tables giving X-ray crystallographic data for **2**, **3a**, and **4**–**6**. These data are available free of charge via the Internet at http://pubs.acs.org.

OM010857K