

Pincer Chromium(II) and Chromium(III) Complexes Supported by Bis(imino)aryl NCN ligands: Synthesis and Catalysis on Isoprene Polymerization

Zhizhou Liu,[†] Wei Gao,^{*,†} Xiaoming Liu,[†] Xuyang Luo,[†] Dongmei Cui,[‡] and Ying Mu^{*,†}

[†]State Key Laboratory for Supramolecular Structure and Materials, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China, and [‡]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, People's Republic of China

Received September 25, 2010

Reactions of 2,6-(ArN=CH)₂C₆H₃Li with CrCl₂(THF)₂ afford two trinuclear bis(imino)aryl NCN pincer Cr(II) complexes {[2,6-(ArN=CH)₂C₆H₃]Cr(μ -Cl)₂}₂Cr [Ar = 2,6-Me₂C₆H₃ (1a), 2,6-Et₂C₆H₃ (1b)], and a mononuclear bis(imino)aryl NCN pincer Cr(II) complex [2,6-(ArN=CH)₂C₆H₃]Cr(μ -Cl)₂Li(THF)₂ [Ar = 2,6-ⁱPr₂C₆H₃ (1c)], respectively. Similar reactions of 2,6-(ArN=CH)₂C₆H₃Li with CrCl₃(THF)₃ produce only mononuclear bis(imino)aryl NCN pincer Cr(II) complexes [2,6-(ArN=CH)₂C₆H₃]CrCl₂(THF) [Ar = 2,6-Me₂C₆H₃ (2a), 2,6-Et₂C₆H₃ (2b), 2,6-ⁱPr₂C₆H₃ (2c)]. X-ray crystallographic analysis reveals that the terminal Cr(II) atoms in 1a and 1b and the Cr(II) atom in 1c possess a distorted trigonal bipyramidal coordination environment with the C_{*ipso*} atom of the pincer ligand and two chloride atoms in the equator and the two imine nitrogen atoms in the apical positions, while the Cr(III) complexes 2a, 2b, and 2c all adopt a distorted octahedral geometry around the chromium metal. Upon activation with trialkylaluminum and [Ph₃C]⁺[B(C₆F₅)₄]⁻, the Cr(III) complexes show high catalytic activity for isoprene polymerization and afford polyisoprene with predominately trans-1,4 units, whereas the Cr(II) complexes are inert under the same conditions.

Introduction

Since the Phillips¹ catalyst and the Union Carbide² catalyst were commercially used in the olefin polymerization industry, a large amount of well-defined chromium complexes with various ligands,³ especially noncyclopentadienyl ligands,⁴ have been synthesized and investigated as catalysts for olefin oligomerization and polymerization. Among these well investigated chromium catalysts, the chromium complexes supported by pincer pyridine derivatives have received considerable attentions due to their unique structural feature and catalytic properties. The bis(imino)pyridine chromium complexes (A in Chart 1) have been reported to show moderate to high catalytic activity for ethylene oligomerization or polymerization depending on the valence of the chromium metal center, the electronic and steric properties of the substituents on the imino N atoms and the polymerization conditions.⁵ The bis(carbene)pyridine Cr(III) complexes (**B** in Chart 1) have been found to show high catalytic activity for ethylene oligomerization upon activation with methylaluminoxane (MAO) and afford α -olefins with

^{*}To whom correspondence should be addressed. E-mail: (W.G.) gw@jlu.edu.cn; (Y.M.) ymu@jlu.edu.cn.

^{(1) (}a) Hogan, J. P.; Banks, R. L. Phillips Petroleum Co., U.S. Patent No. 2825721, 1958. (b) Hogan, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2637. (c) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2621. (d) Karol, F. J.; Brown, G. L.; Davison, L. M. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 413.

^{(2) (}a) Karapinka, G. L. Union Carbide Corp., DE 1,808,388, 1970.
(b) Karapinka, G. L. Union Carbide Corp., US 3,709,853, 1973.

^{(3) (}a) Moulin, J. O.; Evans, J.; McGuinness, D. S.; Reid, G.; Rucklidge, A. J.; Tooze, R. P.; Tromp, M. Dalton Trans. 2008, 1177. (b) Wass, D. F. Dalton Trans. 2007, 816. (c) Zhang, S.; Jie, S.; Shi, Q.; Sun, W.-H. J. Mol. Catal A: Chem. 2007, 276, 174. (d) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. J. Am. Chem. Soc. 2005, 127, 10166. (e) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J.; Williams, D. J. J. Am. Chem. Soc. 2005, 127, 11037. (f) McGuinness, D. S.; Rucklidge, A. J.; Tooze, R. P.; Slawin, A. M. Organometallics 2007, 26, 2561. (g) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. Organometallics 2005, 24, 552. (h) MacAdams, L. A.; Kim, W. -K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. Organometallics 2002, 21, 952. (i) Small, B. L.; Carney, M. J.; Holman, D. M.; O'Rourke, C. E.; Halfen, J. A. Macromolecules 2004, 37, 4375. (j) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Duchateau, R. Organometallics
 2007, 26, 3201. (k) Zhang, W.; Sun, W. –H.; Tang, X.; Gao, T.; Zhang, S.; Hao, P.; Chen, J. J. Mol. Catal A: Chem. 2007, 265, 159. (l) García-Orozco, I.; Quijada, R.; Vera, K.; Valderrama, M. J. Mol. Catal A: Chem. 2006, 260, 70. (m) McGuinness, D. S.; Gibson, V. C.; Wass, D. F.; Steed, J. W. J. Am. Chem. Soc. 2003, 125, 12716. (n) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P.; Budzelaar, P. H. J. Am. Chem. Soc. 2002, 124, 12268.

^{(4) (}a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

^{(5) (}a) Esteruelas, M. A.; López, A. M.; Méndez, L.; Oliván, M.; Oñate, E. Organometallics 2003, 22, 395. (b) Small, B. L.; Carney, M. J.; Holman, D. M.; O'Rourke, C. E.; Halfen, J. A. Macromolecules 2004, 37, 4375. (c) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P.; Budzelaa, P. H. J. Am. Chem. Soc. 2002, 124, 12268. (d) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Duchateau, R. Organometallics 2007, 26, 3201.

⁽⁶⁾ McGuinness, D. S.; Gibson, V. C.; Wass, D. F.; Steed, J. W. J. Am. Chem. Soc. 2003, 125, 12716.



80-93% selectivities.⁶ The bis(oxazolinyl)pyridine Cr(III) complexes (**C** in Chart 1) were reported to catalyze ethylene polymerization and ethylene/1-hexene copolymerization in the presence of MAO.⁷ The bis(benzimidazolyl)pyridines Cr(III) complexes (**D** in Chart 1) were also reported to show high catalytic activities for ethylene oligomerization and polymerization with MAO as the cocatalyst, and high molecular weight polyethylene was produced in the presence of Et₂AlCl.⁸

In the literatures, PCP, SCS, and diaminoaryl NCN pincer ligands were widely used in nickel and platinum complexes.⁹ Recently, the bis(imino)aryl NCN pincer ligands with more rigid and conjugated framework have received considerable attention. Ir, Pt, and Pd pincer complexes with the bis-(imino)aryl NCN ligands have been developed and investigated as catalysts for transfer hydrogenation of ketones, Heck coupling and C–C bond formation reactions.^{10–15} More recently, bis(imino)aryl NCN pincer lanthanide complexes were found to exhibit high catalytic activity and *cis*-1,4 selectivity for butadiene and isoprene polymerization.¹⁶ The structural similarity between the bis(imino)aryl NCN and bis(imino)pyridine NNN pincer ligands, and the good catalytic performance of the pincer lanthanide complexes intrigued us to develop bis(imino)aryl pincer chromium complexes and investigate their catalytic behaviors for olefin

(b) Albrecht, M.; van Koten, G. Angew. Chem., Int. Ed. 2001, 40, 3750.

(10) (a) Parshall, G. Acc. Chem. Res. **1970**, *3*, 139. (b) Dehand, J.; Preffer, M. Coord. Chem. Rev. **1976**, *18*, 327. (c) Bruce, M. Angew. Chem., Int. Ed. **1977**, *89*, 75. (d) Omae, I. Chem. Rev. **1979**, *79*, 287. (e) Omae, I. Coord. Chem. Rev. **1986**, *86*, 451. (f) Shilov, A.; Shul'pin, G. Chem. Rev. **1997**, *97*, 2897. (g) Albrecht, M.; Koten, G. Angew. Chem., Int. Ed. **2001**, *40*, 3750.

(11) Beley, M.; Collin, J.; Sauvage, J. Inorg. Chem. 1993, 32, 4539.

(12) Cámpora, J.; Palma, P.; del Río, D.; Conejo, M. M.; Alvarez, E. Organometallics 2004, 23, 5653.

(13) (a) Takenaka, K.; Minakawa, M.; Uozumi, Y. J. Am. Chem. Soc.
2005, 127, 12273. (b) Hossain, M.; Lucarini, S.; Powell, D.; Bowman-James, K. Inorg. Chem. 2004, 43, 7275. (c) Kjellgren, J.; Sundén, H.; Szabó, K. J. Am. Chem. Soc. 2005, 127, 1787.

(14) (a) Hoogervorst, W.; Koster, A.; Lutz, M. Organometallics 2004, 23, 1161. (b) Hoogervorst, W.; Elsevier, C.; Lutz, M.; Spek, A. Organometallics 2001, 20, 4437.

polymerization. Herein we wish to report the synthesis and characterization of several new bis(imino)aryl pincer Cr(II) and Cr(III) complexes {[2,6-(ArN=CH)₂C₆H₃]Cr(μ -Cl)₂}₂Cr [Ar=2,6-Me₂C₆H₃(**1a**), 2,6-Et₂C₆H₃(**1b**)], [2,6-(ArN=CH)₂ C₆H₃]Cr(μ -Cl)₂Li(THF)₂ [Ar = 2,6-Pr₂C₆H₃(**1c**)], and [2,6-(ArN=CH)₂C₆H₃]CrCl₂(THF) [Ar = 2,6-Me₂C₆H₃(**2a**), 2,6-Et₂C₆H₃(**2b**), 2,6-Pr₂C₆H₃(**2c**)], as well as their catalytic behaviors for isoprene polymerization.

Results and Discussion

Synthesis and Characterization of the Pincer Bis(imino)aryl Cr(II) Complexes. The new pincer bis(imino)aryl Cr(II) complexes were synthesized in moderate yields (55-65%) via the lithium salt elimination reaction of 2,6-(ArN=CH)₂ C₆H₃Li [Ar = 2,6-Me₂C₆H₃ (LiLa), 2,6-Et₂C₆H₃ (LiLb), 2,6-ⁱ Pr₂C₆H₃ (LiLc)] with CrCl₂(THF)₂ in THF as shown in Scheme 1. Such lithium salt elimination reaction has been successfully applied in the synthesis of bis(imino)aryl NCN pincer complexes of aluminum, zinc, and lanthanide.¹⁶ The lithium salts of ligands LiLa–LiLc were prepared *in situ* by treatment of the ligand precursors BrLa–BrLc with ⁿBuLi in THF at -78 °C.

Complexes 1a-1c were all characterized with elemental analyses, IR spectroscopy and single crystal X-ray crystallography. No informative NMR spectra of these complexes were obtained due to their paramagnetic nature. The single crystals of complexes 1a-1c suitable for X-ray structural determination were grown from THF/hexane mixed solvent. The molecular structures of 1a-1c, together with their selected bond distances and angles, are shown in Figures 1-3, respectively. Their crystallographic data are summarized in Table 1. Complexes 1a and 1b were found to exist as a trinuclear form in which two [2,6-(ArN=CH)₂C₆H₃]Cr(µ-Cl) moieties are linked by a $Cr(\mu$ -Cl)₂ molecule through the bridging chloride atoms. The internal Cr atom in complexes **1a** and **1b** is lying on a C_2 axial and the geometry around the internal Cr atom could be described as a distorted square planar. The Cr-Cl bond distances for the internal Cr atom are 2.3905(7) and 2.3702(7) Å in 1a, 2.3992(9) and 2.3723(10) A in **1b**. These data are close to those of 2.375(2) - 2.417(3) A in complex $[Ar'Cr(\mu-Cl)]_2$ $(Ar' = C_6H_3-2, 6-(C_6H_3-2, 6-P_1r_2)_2)^{17}$ The geometry around the terminal Cr atoms in both complexes are distorted trigonal bipyramidal with the two chloride atoms and the C_{ipso} in the equator and two imine nitrogen atoms in the apical positions. The terminal Cr atoms in complexes 1a and 1b are essentially in the NCN coordination plane. The Cr $-C_{inso}$ bond distances of 1.992(3) Å in **1a** and 1.985(4) Å in **1b** are slightly shorter than those in [Ar'Cr(μ -Cl)]₂ (Ar' = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂) (2.041(3) Å)¹⁷ and [Ar'Cr(μ -NMe₂)₂]₂Cr (2.123(2) Å).¹⁸ The N-Cr bond lengths of 2.170(2) and 2.181(2) Å in 1a, 2.178(3) and 2.179(3) Å in 1b are comparable to those in similar bis-(imino)pyridine Cr(III) complexes.^{5a} The terminal Cr-Cl bond lengths of 2.5238(8) and 2.4965(8) Å in 1a, 2.5336(13) and 2.4933(13) Å in **1b** are obviously longer than that of 2.360 Å (av) in bis(imino)pyridine Cr(II) complexes^{5d} and those in the Cr(III) complexes 2a-2c (2.2915(8)-2.3205(7) A). The mononuclear Cr(II) complex 1c also adopts a distorted trigonal bipyramidal geometry around the Cr(II)

 ⁽⁷⁾ Esteruelas, M. A.; López, A. M.; Méndez, L.; Oliván, M.; Oñate,
 E. New J. Chem. 2002, 26, 1542.

⁽⁸⁾ Zhang, W.; Sun, W. -H.; Zhang, S.; Hou, J.; Wedeking, K.;
Schultz, S.; Fröhlich, R.; Song, H. *Organometallics* 2006, *25*, 1961.
(9) (a) van der Boom, M. E.; Milstein, D. *Chem. Rev.* 2003, *103*, 1759.

^{(15) (}a) Hoogervorst, W.; Koster, A.; Lutz, M.; Spek, A.; Elsevier, C. *Organometallics* **2004**, *23*, 4550. (b) Oakley, S.; Coogan, M.; Arthur, R. *Organometallics* **2007**, *26*, 2285.

⁽¹⁶⁾ Gao, W.; Cui, D. J. Am. Chem. Soc. 2008, 130, 4984.

⁽¹⁷⁾ Sutton, A. D.; Ngyuen, T.; Fettinger, J. C.; Olmstead, M. M.; Long, G. J.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 4809.

⁽¹⁸⁾ Ni, C.; Long, G. J.; Grandjean, F.; Power, P. P. *Inorg. Chem.* **2009**, *48*, 11594.









Figure 1. Perspective view of **1a** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)-C(1) 1.992(3), Cr(1)-N(1) 2.170(2), Cr(1)-N(2) 2.181(2), Cr(1)-Cl(1) 2.5238(8), Cr(1)-Cl(2) 2.4965(8), Cr(2)-Cl(1) 2.3905(7), Cr(2)-Cl(2) 2.3702(7), Cl(1)-Cr(1)-Cl2 82.11(3), N(1)-Cr(1)-N(2) 151.87(8). Cl(1)-Cr(2)-Cl(2) 87.68(2).

atom, which becomes five-coordinated through combining with a LiCl(THF)₂ moiety. The planes of the two *N*-aryl rings in **1c** are nearly orthogonal to the NCN plane with angles of 82.18(19) and 88.63(24)°, respectively. The chromium atom is essentially in the NCN plane with a deviation of 0.0902(46) Å. The bond distances of Cr-C, Cr-Cl, and Cr-N are all comparable to those in complexes **1a** and **1b**. The Cl-Cr_{distal}-Cl angle of 91.70(6)° in **1c** is much larger than those in **1a** (82.11(3)°) and in **1b** (82.52(4)°), while the N-Cr-N angle of 151.50(18)° in **1c** is close to the ones of 151.87(8)° in **1a** and 151.74(13)° in **1b**. The imine C=N bond lengths ranging from 1.281(3) to 1.304(4) Å are comparable to those in analogous lanthanide and platinum complexes.^{16,19}

Synthesis and Characterization of the Pincer Bis(imino)aryl Cr(III) Complexes. The pincer bis(imino)aryl Cr(III) complexes 2a-2c were synthesized in a similar procedure to that for the Cr(II) complexes 1a-1c as shown in Scheme 2. Reactions of the *in situ* formed lithium salts of the ligands with CrCl₃(THF)₃ in THF produced complexes 2a-2c in





Figure 2. Perspective view of **1b** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)-C(1) 1.985(4), Cr(1)-N(1) 2.178(3), Cr(1)-N(2) 2.179(3), Cr(1)-Cl(1) 2.5336(13), Cr(1)-Cl(2) 2.4933(13), Cr(2)-Cl(1) 2.3992(9), Cr(2)-Cl(2) 2.3723(10), Cl(1)-Cr(1)-Cl(2) 82.52(4), N(1)-Cr(1)-N(2) 151.74(13), Cl(1)-Cr(2)-Cl(2) 88.02(4).

morderate yields. Complexes 2a-2c were also characterized with elemental analyses, IR spectroscopy and single crystal X-ray crystallography. Single crystals of these complexes suitable for X-ray structural determination were grown from THF/hexane or CH₂Cl₂/hexane mixed solvent. The molecular structures of complexes 2a-2c, together with their selected bond distances and angles, are shown in Figures 46, respectively. The crystallographic data are summarized in Table 1. Complexes 2a, 2b, and 2c are isostructral and the geometry around the six coordinated chromium atom in these complexes could be described as a distorted octahedron with a tridentate pincer NCN ligand, two chlorides and a coordinated THF molecule. Similar to the Cr(II) complexes, the Cr(III) atoms in these complexes are essentially in the bis(imino)aryl NCN plane and the planes of the N-aryl rings are almost vertical to the NCN plane. The $Cr-C_{ipso}$ bond distances of 1.963(2) Å in 2a, 1.957(2) Å in 2b, and 1.960(4) Å in 2c are slightly shorter than those in Cr(II) complexes 1a-1c, but remarkably shorter than the ones in Cr(III) complexes $[Cp*Cr(C_6F_5)(\mu-Cl)]_2$ (2.109(6) Å) and $[Cp*Cr-(C_6F_5)(\mu-CH_3)]_2$ (2.1375(19) Å).²⁰ The Cr-Cl bond distances of 2.3160 (av) Å in 2a, 2.3023 (av) Å in 2b, and 2.3087 (av) Å in 2c are comparable to those in the bis-(imino)pyridine Cr(III) complexes, ^{5a,d} but shorter than those

⁽²⁰⁾ Ganesan, M.; Gabbaï, F. P. Organometallics 2004, 23, 4608.



Figure 3. Perspective view of 1c with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)-C(1) 1.985(6), Cr(1)-N(1) 2.200(4), Cr(1)-N(2) 2.186(5), Cr(1)-Cl(1) 2.4875(16), Cr(1)-Cl(2) 2.4624(16), Cl(1)-Li(1) 2.306(12), Cl(2)-Li(1) 2.372(11), O(1)-Li(1) 1.872 (13), O(2)-Li(1) 1.973(13), Cl(1)-Cr(1)-Cl(2) 91.70(6), Cl(1)-Li(1)-Cl(2) 98.8(4), N(1)-Cr(1)-N(2) 151.50(18), O(1)-Li(1)-O(2) 100.3(6).

in Cr(II) complexes 1a-1c (2.4624(16)-2.5338(8) Å). The two chlorides arrange in *trans*-positions to form a large Cl-Cr-Cl angle of 178.83(3)° in **2a**, 177.34(3)° in **2b**, and 179.17(4)° in **2c**.

Isoprene Polymerization Studies. Polybutadiene and polyisoprene have been the most widely used synthetic rubbers. Methods for the polymerization of conjugated dienes have been known for a long time, but the true breakthrough was achieved by stereospecific polymerization of conjugated dienes with transition metal-based coordination catalysts.²¹ Homogeneous Ziegler-Natta catalyst systems composed of complexes of various transition metals, such as Ti, 22,24d V, 23 Fe, 24 Co, 24d,25 Ni, 24d,26 and Nd, 27 and the coactivators aluminum alkyls or the aluminum alkyl chloride have been extensively investigated. Some chromium((III) systems such as Cr(acac)₃/AlEt₃, Cr(allyl)₃/MAO, Cr(allyl)₂Cl//MAO, and Cr(acac)₃/MAO have been reported to polymerize butadiene to polybutadiene with predominantly 1,2- or cis-1,4-units, though their catalytic activities are rather low.^{22f,23a,28} Recently some Cr(II) complexes supported by phosphine ligands, such as $\operatorname{CrCl}_2(\operatorname{dmpe})_2$ (dmpe = 1,2-bis(dimethylphosphino) ethane)²⁹ and $\operatorname{Cr}(\operatorname{CH}_3)_2(\operatorname{dmpe})_2$,²⁹ were found to show high catalytic activity for butadiene polymerization in the presence of MAO, affording predominantly 1,2-polybutadiene. The isoprene polymerization by chromium complexes is rare so far. Only some Cr-allyl,^{28b-d} derivatives and $CrCl_2(dmpe)_2^{29}$ were known to show low catalytic activity for isoprene polymerization to form polyisoprene with predominantly 3,4-units, and some chromium complexes supported by N,N-bis-(diarylphosphino)amine³⁰ were reported to display moderate catalytic activity for isoprene trimerization.

All new chromium complexes 1a-1c, 2a-2c were evaluated as catalysts for isoprene polymerization. The polymerization data are summarized in Table 2. Upon activation with trialkylaluminum, all complexes were found to be inactive toward isoprene polymerization and no polymer was obtained even the polymerization experiments were carried out at high temperatures and for long times, which may be attributed to the low Lewis acidity of the resulted alkyl chromium complexes. The Cr(II) complexes 1a-1c are still inactive even they were activated with $AlR_3/Ph_3C^+B^-(C_6F_5)_4^-$ or MAO. Such a result is understandable considering that the cationic species formed from these complexes during the activation reaction carries no alkyl group and thus is unable to form a polymer chain though the isoprene molecule can coordinate to the metal center as shown in Scheme 3.

The Cr(III) complexes 2a-2c show moderate to high catalytic activity and good *trans*-1,4 selectivity at room temperature when activated with AlR₃/Ph₃C⁺B(C₆F_{5)4⁻}. Complex **2b** show higher activities than that of complex **2a** and **2c** under similar conditions, and a complete conversion could

⁽²¹⁾ Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 4, Part II, pp 53–108.

^{(22) (}a) Natta, G.; Porri, L.; Carbonaro, A.; Stoppa, G. Makromol. Chem. 1964, 77, 114. (b) Porri, L.; Giarrusso, A.; Ricci, G. Makromol. Chem., Macromol. Symp. 1991, 48/49, 239. (c) Natta, G.; Porri, L.; Carbonaro, A. Makromol. Chem. 1964, 77, 126. (d) Copper, W.; Vaughan, G. Prog. Polym. Sci. 1967, 1, 128. (e) Razuvaev, G. A.; Minsker, K. S.; Fedoseeva, G. T.; Savel'ev, I. A. Vysokomol. Soed. 1959, 1, 1691. (f) Bawn, C. E.; North, A. M.; Walker, J. S. Polymer 1964, 5, 419. (g) Cucinella, S. Chim. Ind. (Milan) 1977, 59, 696.

^{(23) (}a) Natta, G.; Porri, L.; Zanini, G.; Palvarini, A. Chim. Ind. (Milan) **1959**, 41, 1163. (b) Natta, G.; Porri, L.; Mazzei, A. Chim. Ind. (Milan) **1959**, 41, 116. (c) Natta, G.; Porri, L.; Corradini, P.; Morero, D. Chim. Ind. (Milan) **1958**, 40, 362. (e) Natta, G.; Porri, L.; Fiore, L.; Zanini, G. Chim. Ind. (Milan) **1958**, 40, 116. (f) Natta, G.; Porri, L.; Carbonaro, A. Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend. **1961**, 31, 189.

^{(24) (}a) Zhang, Z. Y.; Zhang, H. J.; Ma, H. M.; Wu, Y. *J. Mol. Catal.* **1982**, *17*, 65. (b) Ricci, G.; Morganti, D.; Sommazzi, A.; Santi, R.; Masi, F. *J. Mol. Catal. A: Chem.* **2003**, *204/205*, 287. (c) Masi, F.; Sommazzi, A.; Santi, R.; Ricci, G.; Pampaloni, G.; Bonsignore, S.; Valenti, S.; Bianchini, C. 2002, WO02 102861 to Polimei Europa. (d) Ricci, G.; Sommazzi, A.; Masi, F.; Ricci, M.; Boglia, A.; Leone, G. *Coord. Chem. Rev.* **2010**, *254*, 661.

⁽²⁵⁾ Porri, L.; Giarrusso, A.; Ricci, G. Makromol. Chem., Makromol. Symp. 1991, 48/49, 239. (b) Copper, W.; Vaughan, G. Prog. Polym. Sci. 1967, 1, 128. (c) Gippin, M. Ind. Eng. Chem., Prod. Res. Dev. 1962, 1, 32. (d) Longiave, C.; Castelli, R. J. Polym. Sci., C 1963, 4, 387. (e) Susa, E. J. Polym. Sci., C 1963, 4, 399. (f) Ashitaka, H.; Ishikawa, H.; Ueno, H.; Nagasaka, A. J. Polym. Sci., Polym. Chem. Ed. 1983, 21, 1853. (g) Ashitaka, H.; Jinda, K.; Ueno, H. J. Polym. Sci., Polym. Chem. Ed. 1983, 21, 1853. (g) Ashitaka, H.; Jinda, K.; Ueno, H. J. Polym. Sci., Polym. Chem. Ed. 1983, 21, 1989.

^{(26) (}a) Longiave, C.; Castelli, R.; Croce, G. F. Chim. Ind. (Milan) **1961**, 43, 625. (b) Sakata, R.; Hosono, J.; Onishi, A.; Ueda, K. Makromol.
Chem. **1970**, 139, 73. (c) Beebe, D. H.; Gordon, C. E.; Thudium, R. N.;
Throckmorton, M. C.; Hanlon, T. L. J. Polym. Chem. Ed. **1978**, 16, 2285.
(27) Shen, Z.; Ouyang, J.; Wang, F.; Hu, Z.; Yu, F.; Qian, B.
J. Polym. Sci., Polym. Chem. Ed. **1980**, 18, 3345. (b) Mazzei, A. Makromol. Chem., Suppl **1981**, 4, 61. (c) Wilson, D. J.; Jenkins, D. K. Polym. Bull. **1992**, 27, 407. (d) Hsieh, H.; Yeh, H. Rubber Chem. Technol. **1985**, 58, 117.
(e) Friebe, L.; Nuyken, O.; Obrecht, W. Adv. Polym. Sci. **2006**, 204, 1. (f)

 ^{(28) (}a) Hiraki, K.; Hirai, H. J. Polym. Sci., Polym. Chem. Ed. 1973,

 ^{11, 901. (}b) Dolgoplosk, B. A.; Tinyakova, E. I.; Stefanovskaya, N. N.;
 Oreshkin, I. A.; Shmonina, V. L. *Eur. Polym. J.* **1974**, *10*, 605. (c) Shmonina,
 V. L.; Stefanovskaya, N. N.; Tinyakova, E. I.; Dolgoplosk, B. A. *Polym. Sci.* U.S.S.R. **1973**, *15*, 733. (d) Oreshkin, I. A.; Tinyakova, E. I.; Dolgoplosk,
 B. A. *Polym. Sci. U.S.S.R.* **1969**, *11*, 2106.

^{(29) (}a) Ricci, G.; Battistella, M.; Porri, L. *Macromolecules* 2001, *34*, 5766. (b) Ricci, G.; Forni, A.; Boglia, A.; Sonzogni, M. *Organometallics* 2004, *23*, 3727. (c) Ricci, G.; Boglia, A.; Motta, T. *J. Mol. Catal. A: Chem.* 2007, *267*, 102.

^{(30) (}a) Bowen, L. E.; Charernsuk, M.; Wass, D. F. *Chem. Commun.* **2007**, 2835. (b) Bowen, L. E.; Charernsuk, M.; Hey, T. W.; McMullin, C. L.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2010**, *39*, 560.

Table 1. Summary of crystallographic data for complexes 1a, 1b, 1c, 2a, 2b, and 2c

	$1a \cdot C_6 H_{14}$	$1b \cdot C_7 H_8$	$1c \cdot C_7 H_8$	2a	2b	2c
formula	C54H60Cl4Cr3N4	C ₆₃ H ₆₄ Cl ₄ Cr ₃ N ₄	C47H57Cl2CrLiN2O2	C ₂₈ H ₃₁ Cl ₂ CrN ₂ O	C ₃₂ H ₃₉ Cl ₂ CrN ₂ O	C37H47Cl4CrN2O
$F_{\rm w}$	1062.86	1174.98	811.79	534.45	590.55	729.57
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	C2/c	C2/c	P2(1)/c	$P\overline{1}$	P2(1)/c	$P\overline{1}$
a (Å)	25.3449(17)	24.9698(12)	12.8943(10)	8.2397(9)	18.866(4)	9.3344(5)
$b(\mathbf{A})$	12.1107(8)	13.2003(6)	11.0704(8)	9.8919(11)	10.216(2)	13.1536(8)
c(Å)	19.9733(14)	20.3508(10)	32.599(3)	16.2560(18)	31.635(6)	16.5930(10)
α (deg)	90	90	90	77.252(2)	90	101.3040(10)
β (deg)	121.8020(10)	119.3960(10)	95.471(2)	86.119(2)	92.74(3)	102.0590(10)
γ (deg)	90	90	90	87.316(2)	90	94.7220(10)
$v(A^3)$	5210.3(6)	5844.2(5)	4632.1(6)	1288.7(2)	6090(2)	1937.5(2)
Z	4	4	4	2	8	2
$\mu ({\rm mm}^{-1})$	0.859	0.773	0.399	0.675	0.578	0.601
R _{int}	0.0346	0.0417	0.0787	0.0155	0.0760	0.0251
GOOF	1.033	1.028	1.035	1.050	1.024	1.033
<i>R</i> 1	0.0398	0.0567	0.0848	0.0396	0.0583	0.0699
w <i>R</i> 2	0.0929	0.1393	0.2159	0.1003	0.1181	0.2068

Scheme 2. Synthesis of the Pincer Bis(imino)aryl Cr(III) Com-



Figure 4. Perspective view of 2a with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)-C(1) 1.963(2), Cr(1)-N(1) 2.1637(19), Cr(1)-N(2) 2.1862(19), Cr(1)-Cl(1) 2.3116(7), Cr(1)-Cl(2) 2.3205(7), Cr(1)-O(1) 2.1232(16), Cl-(1)-Cr(1)-Cl(2) 178.83(3), N(1)-Cr(1)-N(2) 155.31(7), C-(1)-Cr(1)-O(1) 177.55(8).

be achieved in only 15 min. This may be attributed to the low stability of the cationic center shielded by the less bulky ligand in **2a**, and more bulky in **2c** hindering the coordination of the monomer. Similar results were also observed in the pincer bis(imino)aryl lanthanide catalyst systems.¹⁶ The 1,4-selectivity of these catalyst systems was also found to be slightly affected by the bulkiness of their ligand and vary in the order of **2a** (86.6%) > **2b** (84.3%) > **2c** (83.7%).

The catalytic activity of these Cr(III) complexes is strongly affected by the trialkylaluminum cocatalyst in the trend of $Al^iBu_3 > AlEt_3 \gg AlMe_3$ (see entries 3, 5, and 6 in Table 2).



Figure 5. Perspective view of **2b** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)-C(1) 1.957(2), Cr(1)-N(1) 2.197(2), Cr(1)-N(2) 2.175(2), Cr(1)-Cl(1) 2.2915(8), Cr(1)-Cl(2) 2.3131(8), Cr(1)-O(1) 2.1515(19), Cl-(1)-Cr(1)-Cl(2) 177.34(3), N(1)-Cr(1)-N(2) 154.89(8), C-(1)-Cr(1)-O(1) 177.19(9).

Such a result seems to be indicative of that a weak interaction between the formed alkyl chromium species and the cocatalyst might benefit the coordination and insertion of isoprene. The low activities of AlMe₃ catalytic system may due to the reduction of Cr(III) to Cr(II) by AlMe₃.³¹ It is found that the catalytic activity of these complexes were affected moderately by the borate or borane cocatalyst in the order of $Ph_{3}C^{+}B(C_{6}F_{5})_{4}^{-} \approx PhMe_{2}NH^{+}B(C_{6}F_{5})_{4}^{-} > B(C_{6}F_{5})_{3}$ (entries 3, 10, 11). It is interesting to note that the type of the borate/borane cocatalyst shows significant influence on the molecular weight of the resultant polymer. The polymers produced from the $Ph_3C^+B(C_6F_5)_4^-$ and $PhMe_2NH^+B$ - $(C_6F_5)_4^-$ activated catalyst systems have similar molecular weight values, which are much higher than the one for the polymer obtained from $B(C_6F_5)_3$ activated catalyst system. When MAO was used as the co catalyst, complex 2b showed low catalytic activity with only 28% monomer conversion in 60 min. However, the resultant polymer was found to be ultrahigh molecular weight and with 90.5% trans-1,4 selectivity

⁽³¹⁾ Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. J. Am. Chem. Soc. 2002, 124, 12268.

(entry 12). The catalytic activities of complex **2b** also show great dependence on the polymerization temperature (entries 3, 13–15). When the polymerization was performed at -20 °C, almost no polymer was obtained. The monomer conversion increases rapidly with the increase in polymerization temperature affording high molecular weight polymer which is insoluble in THF. In addition, the polymerization was also tried in different solvents, and obvious solvent effect was observed. The catalytic activity of the **2b**/Al^{*i*}Bu₃/Ph₃C⁺B-(C₆F₅)₄⁻ system in different solvents changes in the order of C₆H₅Cl > toluene > *n*-hexane. However, high molecular



Figure 6. Perspective view of 2c with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)-C(1) 1.960(4), Cr(1)-N(1) 2.210(3), Cr(1)-N(2) 2.201(3), Cr(1)-Cl(1) 2.3143(10), Cr(1)-Cl(2) 2.3031(10), Cr(1)-O(1) 2.127(3), Cl(1)-Cr(1)-Cl(2) 179.17(4), N(1)-Cr-(1)-N(2) 154.66(11), C(1)-Cr(1)-O(1) 178.74(13).

weight polymers were obtained from toluene and *n*-hexane due to low solubility of the catalyst in these solvents.

In summary, we have synthesized and characterized a series of new chromium(II) and chromium(III) complexes supported by bis(imino)aryl pincer ligands via lithium salt elimination reaction. Upon activation with trialkylaluminum and borate cocatalyst, the Cr(III) complexes show high catalytic activity for isoprene polymerization and afford polyisoprene with predominately *trans*-1,4 units, whereas the Cr(II) complexes are inert under the same conditions. The catalytic performance of these Cr(III) complexes were found to be influenced by the *ortho*-substituent of the *N*-aryl ring, trialkylaluminum, and the type of the borate/borane cocatalyst.

Experimental Section

General Considerations. All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene and hexane were dried over sodium metal and distilled under nitrogen. Elemental analyses were performed on a Varian EL microanalyzer; infrared spectra were recorded as KBr disks with a Nicolet Avatar 360. NMR spectra were carried out on Varian 300 Hz instrument at room temperature in CDCl₃ solution for ligands and polymers. The molecular weight and molecular weight distribution of the polymers were measured by TOSOH HLC 8220 GPC at 40 °C using THF as eluent against polystyrene standards. The ligands were synthesized according to the literature. 2,6-Dimethylaniline, 2,6-diethylaniline (90%), and 2,6-diisopropylaniline were bought from Aldrich Chemical Co. and used without further purification.

{[2,6-(2,6-Me₂C₆H₃N=CH)₂C₆H₃]Cr (μ -Cl)₂}₂Cr (1a). A hexane solution of ⁿBuLi (0.66 mL, 1.05 mmol) was added dropwise to a THF (20 mL) solution of 2,6-(2,6-Me₂C₆H₃N=CH)₂C₆H₃-1Br (0.42 g, 1.00 mmol) at -78 °C. The mixture was stirred for 4 h

Table 2. Polymerization of Isoprene under Various Conditions^a



entry	catal	Al/Cr	AlR ₃	$T_{\rm p}(^{\circ}{\rm C})$	time (min)	yield (%)	$M_{\rm n}^{\ b}$ (× 10 ⁴)	PDI	microstructure ^c (%)		
									trans-1,4-	3,4-	$eff.^{d}(\%)$
1	1a-1c	20	Al ⁱ Bu ₃	20	120						
2	2a	20	Al ⁱ Bu ₃	20	60	14.6	1.15	1.029	86.6	13.4	86.4
3	2b	20	Al ⁱ Bu ₃	20	15	100	96.8	2.096	84.3	19.7	7.0
4	2c	20	Al ⁱ Bu ₃	20	15	95.5	58.8	2.460	83.7	16.3	11.1
5	2b	20	AMe ₃	20	120						
6	2b	20	AlEt ₃	20	120	55.7	36.5	2.305	80.0	20.0	10.4
7	2b	5	Al ⁱ Bu ₃	20	60						
8	2b	10	Al ⁱ Bu ₃	20	15	50.4	82.7	2.176	79.7	20.3	4.2
9	2b	40	Al ⁱ Bu ₃	20	15	100	104.9	1.812	86.2	13.8	6.5
10^e	2b	20	Al ⁱ Bu ₃	20	15	96.8	88.1	2.179	83.3	16.7	6.6
11^{f}	2b	20	AliBu ₃	20	15	85.5	8.67	2.647	83.0	17.0	76.0
12	2b	100	MAO	20	60	28.0	149.6	1.649	90.5	8.5	1.2
13	2b	20	Al ⁱ Bu ₃	-20	60						
14	2b	20	Al ⁱ Bu ₃	0	60	27.2	72.2	2.197	81.7	18.3	2.5
15	2b	20	Al ⁱ Bu ₃	40	15	100	N/A^i	N/A^i	86.2	13.8	4.7
16^g	2b	20	Al ⁱ Bu ₃	20	15	93.6	N/A^i	$\dot{N/A^i}$	80.3	19.7	
17^{h}	2b	20	Al ⁱ Bu ₃	20	30	50.3	N/A^i	\dot{N}/A^{i}	85.1	14.9	

^{*a*} Unless otherwise specified, the polymerization reactions used C₆H₅Cl (10 mL), complex (10 μ mol), and isoprene (10 mmol). [Cr]₀/[AlR₃]₀/ [Ph₃C⁺B(C₆F₅)₄⁻]₀ = 1:20:1. ^{*b*} Determined by gel permeation chromatography (GPC) with respect to a polystyrene standard. ^{*c*} Determined by ¹H NMR spectrum. ^{*d*} Catalyst efficiency = M_n (calculated)/ M_n (measured). ^{*e*} PhMe₂NH⁺B(C₆F₅)₄⁻ used as cocatalyst. ^{*f*}(C₆F₅)₃ used as cocatalyst. ^{*g*} Used as the solvent. ^{*h*} Used as the solvent. ^{*i*} The molecular weight was not measured because of low solubility of the polymers in THF.



Scheme 3. Proposed Mechanism for Isoprene Polymerization by Cr(II) and Cr(III) Complexes

before the addition of CrCl₂(THF)₂ (0.27 g, 1.00 mmol). The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. The solvent was removed under reduce pressure and the residue was treated with toluene, after evaporation of the toluene to dryness, the product was obtained as purple powder. Yield: 0.18 g, (55% based on CrCl₂(THF)₂) Crystals of **1a** suitable for X-ray structural determination was grown in THF/hexane mixed solvent. Anal. Calcd for C₄₈H₄₆Cl₄Cr₃N₄: C, 59.03; H, 4.75; N, 5.74. Found: C, 59.21; H, 4.88; N, 5.57. IR (KBr): ν (cm⁻¹) 2950 s, 2330 w, 1630 s, 1610 s, 1550 m, 1470 m, 1380 w, 1290 w, 1260 w, 1230 w, 1180 w, 1110 w, 1060 m, 1030 w, 984 w, 914 w, 860 m, 768 m, 714 w, 687 w, 505 m.

 $\{[2,6-(2,6-Et_2C_6H_3N=CH)_2C_6H_3]Cr(\mu-Cl)_2\}_2Cr$ (1b). A hexane solution of "BuLi (0.66 mL, 1.05 mmol) was added dropwise to a THF (20 mL) solution of 2,6-(2,6-Et₂C₆H₃N=CH)₂C₆H₃-1-Br (0.48 g, 1.00 mmol) at -78 °C. The mixture was stirred for 4 h before the addition of CrCl₂(THF)₂ (0.27 g, 1.00 mmol). The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. The solvent was removed under reduce pressure and the residue was treated with toluene, after evaporation of the toluene to dryness, the product was obtained as blue powder. Yield: 0.22 g, (59% based on CrCl₂(THF)₂) Crystals of 1b suitable for X-ray structural determination was grown in THF/hexane mixed solvent. Anal. Calcd for C₅₆H₆₂Cl₄Cr₃N₄: C, 61.77; H, 5.74; N, 5.15. Found: C, 62.11; H, 5.89; N, 5.11. IR (KBr): ν (cm⁻¹) 2960 s, 2870 s, 1640 s, 1610 m, 1590 m, 1550 m, 1450 m, 1390 m, 1370 m, 1170 m, 1100 w, 1050 w, 980 w, 856 w, 795 w, 760 m, 714 w, 687 w, 525 m.

[2,6-(2,6-^{*i*}Pr₂C₆H₃N=CH)₂C₆H₃]Cr(μ -Cl)₂Li(THF)₂ (1c). Following the same procedure described for the preparation of 1a, treatment of 2,6-(2,6-^{*i*}Pr₂C₆H₃N=CH)₂C₆H₃-1-Br (0.53 g, 1.00 mmol) with "BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then *in situ* adding CrCl₂(THF)₂ (0.27 g, 1.00 mmol) yielded complex 1c as blue powder (0.46 g, 64%). Crystals of 1c suitable for X-ray structural determination was grown in THF/hexane mixed solvent. Anal. Calcd for C₄₀H₅₅Cl₂CrLiN₂O₂: C, 66.20; H, 7.64; N, 3.86. Found: C, 66.34; H, 7.60; N, 3.81. IR (KBr) ν (cm⁻¹): 3060 w, 2960 s, 2920 s, 2870 m, 1640 s, 1540 s, 1450 s, 1380 w, 1360 w, 1320 w, 1250 w, 1160 w, 1100 w, 1060 w, 930 w, 879 w, 798 w, 756 w, 694 w, 517 w.

 $[2,6-(2,6-Me_2C_6H_3N=CH)_2C_6H_3]$ CrCl₂THF (2a). A hexane solution of ⁿBuLi (0.66 mL, 1.05 mmol) was added dropwise to a THF (20 mL) solution of 2, 6-(2,6-Me_2C_6H_3N=CH)_2C_6H_3-1-Br

(0.42 g, 1.00 mmol) at -78 °C. The mixture was stirred for 4 h before the addition of CrCl₃(THF)₃ (0.45 g, 1.20 mmol). The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. Removal of the volatiles under reduced pressure, extracting the residue with toluene and evaporating the solvent to dryness afforded the product as green powder. Yield: 0.34 g, (64%) Crystals of **2a** suitable for X-ray structural determination was grown in THF/hexane mixed solvent. Anal. Calcd for C₂₈H₃₁Cl₂CrN₂O: C, 62.92; H, 5.85; N, 5.24. Found: C, 62.84; H, 5.88; N, 5.17. IR (KBr): ν (cm⁻¹) 3414 s, 3072 w, 2960 m, 2955 m, 2926 m, 1585 m, 1535 m, 1465 m, 1380 w, 1350 w, 1307 w, 1234 w, 1172 s, 1095 s, 1056 m, 1025 m, 979 w, 917 w, 871 m, 856 m, 775 s, 713 m, 636 w, 586 w, 501 w.

[2,6-(2,6-Et₂C₆H₃N=CH)₂C₆H₃]CrCl₂THF (2b). Following the same procedure described for the preparation of 2a, treatment of 2,6-(2,6-Et₂C₆H₃N=CH)₂C₆H₃-1-Br (0.48 g, 1.00 mmol) with ^{*n*}BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then *in situ* adding CrCl₃(THF)₃ (0.45 g, 1.20 mmol) yielded complex 2b as green powder (0.38 g, 64%). Crystals of 2b suitable for X-ray structural determination was grown in CH₂Cl₂/hexane mixed solvent. Anal. Calcd for C₃₂H₃₉Cl₂CrN₂O: C, 65.08; H, 6.66; N, 4.74. Found: C, 65.12; H, 6.47; N, 4.69. IR (KBr): ν (cm⁻¹) 3405 s, 3050 s, 2967 s, 2926 s, 2875 m, 1640 m, 1592 s, 1535 s, 1450 s, 1369 m, 1349 m, 1253 w, 1230 m, 1168 s, 1107 m, 1056 m, 1029 m, 983 w, 914 w, 875 m, 856 m, 798 m, 752 m, 717 m, 582 w, 501 w.

[2,6-(2,6-ⁱPr₂C₆H₃N=CH)₂C₆H₃]CrCl₂THF (2c). Following the same procedure described for the preparation of 2a, treatment of 2,6-(2,6-ⁱPr₂C₆H₃N=CH)₂C₆H₃-1-Br (0.53 g, 1.00 mmol) with "BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then *in situ* adding CrCl₃(THF)₃ (0.45 g, 1.20 mmol) yielded 2c as green powder (0.39 g, 60%). Crystals of 2c suitable for X-ray structural determination was grown in CH₂Cl₂/hexane mixed solvent. Anal. Calcd for C₃₆H₄₇Cl₂CrN₂O: C, 66.86; H, 7.33; N, 4.33. Found: C, 66.92; H, 7.27; N, 4.19. IR (KBr): ν (cm⁻¹) 3058 s, 2950 s, 2865 s, 1631 w, 1592 m, 1538 s, 1458 s, 1438 s, 1380 m, 1357 m, 1326 m, 1230 w, 1168 s, 1103 m, 1056 m, 1029 m, 979 w, 929 w, 871 m, 852 m, 802 m, 806 w, 755 w, 717 w.

Isoprene Polymerization Experiments. General procedure for isoprene polymerization: In a typical polymerization experiment C_6H_5Cl (10 mL) isoprene (1 mL, 10 mmol), and 200 μ mol AlR₃ were added into a 25 mL flask. Then complex **2b** (10 μ mol) and Ph₃C⁺B(C₆F₅)₄⁻ (10 μ mol) were added to initiate the

polymerization. After a designated time, methanol was injected into the system to quench the polymerization. The mixture was poured into a large quantity of methanol to precipitate the white solids. Filtered and dried under vacuum at 40 °C for 24 h polyisoprene was given at a constant weight (0.68 g, 100%).

Crystal Structure Determination. The crystals were mounted on a glass fiber using the oil drop. Data obtained with the $\omega - 2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods, while further refinement with full-matrix least-squares on F^2 was obtained with the SHELXTL program package [100]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Acknowledgment. We thank the National Natural Science Foundation of China for financial support (Nos. 20904013 and 20772044).

Supporting Information Available: X-ray crystallographic data and refinements for complexes **1a**, **1b**, **1c**, **2a**, **2b**, and **2c** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.