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Chromium Complexes with Acenaphthene Imine Derivative Ligands Synthesis and Catalysis on Diene Polymerization

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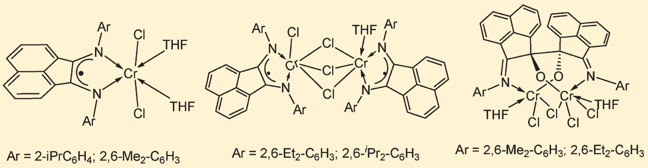
S *Supporting Information*

ABSTRACT: Treatment of the bis(arylimino)acenaphthene (BIAN) ligands with $CrCl_2(THF)_2$ in THF affords mononuclear complexes of $^{Ar}BIANCrCl_2(THF)_2$ (**3a**, Ar = 2-$^iPrC_6H_4$; **3b**, Ar = 2,6-$Me_2C_6H_3$) and chlorine-bridging dinuclear complexes $^{Ar}BIANCrCl(\mu\text{-}Cl)_3Cr(THF)^{Ar}BIAN$ (**3c**, Ar = 2,6-$Et_2C_6H_3$; **3d**, Ar = 2,6-$^iPr_2C_6H_3$). The molecular structures of **3b**−**3d** were characterized by X-ray diffraction analysis, and all the chromium atoms are in octahedral geometries. Similar reactions of *N*-(arylimino)acenaphthenones with $CrCl_2(THF)_2$ afford the dinuclear chromium complexes with 1,1′-bis(2-aryliminoacenaphthene-1-olate) tetradentate ligands $ArBIAOCr_2Cl_4(THF)_2$ (**4b**, Ar = 2,6-$Me_2C_6H_3$; **4c**, Ar = 2,6-$Et_2C_6H_3$) via a pinacol cross-coupling reaction. Upon activation with MAO, these complexes show moderate-to-high activities in butadiene and isoprene polymerization, affording a *cis*-1,4-enriched polymer.



1. INTRODUCTION

Polybutadiene (PB) and polyisoprene (PIP) have been the most widely used synthetic rubbers.[1] In the 1950s, the diene polymers were produced with Alfin catalysts, and the polymer features a high molecular weight and low regularity.[2] The high regularity of the polymer was achieved by stereospecific polymerization of conjugated dienes with transition-metal-based coordination catalysts.[3] Homogeneous Ziegler−Natta catalyst systems composed of complexes of rare earth metals[4] or transition metals, such as Ti,[5,7d] V,[6] Fe,[7] Co,[8,7d] and Ni,[9,7d] and the coactivators aluminum alkyls or the aluminum alkyl chloride have been extensively investigated. The chromium-based catalysts have received special attention due to their specific polymerization of dienes.[10] Some chromium(III) systems, such as $Cr(acac)_3/AlEt_3$, $Cr(allyl)_3$/MAO, $Cr(allyl)_2Cl$/MAO, and $Cr(acac)_3$/MAO, have been reported to polymerize butadiene to PB with predominant 1,2- or *cis*-1,4 units.[5f,6a,11] The chromium(III) complexes with bis(pyrazolyl)pyridine[12] and bis(benzimidazolyl)amine[13] exhibit high activities and high *trans*-1,4 selectivities in butadiene polymerization. Some Cr(II) complexes supported by phosphine ligands, such as $CrCl_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane)[14] and $Cr(CH_3)_2(dmpe)_2$,[14] were found to show high catalytic activity for butadiene polymerization in the presence of MAO, affording 1,2-enriched polybutadiene. The isoprene polymerization initiated by chromium complexes is rare so far. Some Cr-allyl[11b−d] derivatives and $CrCl_2(dmpe)_2$[14] were known to show low activities for isoprene polymerization, producing PIP with predominant 3,4-units, and some chromium complexes supported by *N*,*N*-bis(diarylphosphino)amine[15] exhibit moderate activities for isoprene trimerization. More recently, we have reported that NCN pincer Cr(III) complexes activated by alkylaluminum and borate show high activities in isoprene polymerization, affording a *trans*-1,4-enriched polymer.[16]

In the past decades, the bis(arylimino)acenaphthene (BIAN) ligands have received considerable attention in coordination chemistry and were widely used in catalysis, such as hydrogenation of alkynes,[17] C−C[18] and C−Sn[19] bond formation, and especially in olefin oligomerization/polymerization.[20] BIAN has the unique properties of combining both the diimine and the naphthalene *p* systems and can act as stronger σ-donors toward the metal. In addition to being used as neutral ligands, BIAN ligands might form stable mono- and di- and possibly even tri- and tetra-anions by electron transfer to their mixed 14-electron imine-naphthalene *p* system.[21] Some transition-metal complexes supported by BIAN ligands in radical-anion or enediamine form were extensively investigated.[22] Recently, Fedushkin has reported the dinuclear chromium complexes that were prepared by reaction of the $CrCl_3$ with the Ar-BIAN enediamide magnesium and, subsequently, elimination of the $MgCl_2$. The bisligated chromium complexes can be prepared by reaction of (dpp-BIAN)Na_2 with $CrCl_3$.[23] In these reactions, the $CrCl_3$ was reduced to Cr(II) by the enediamide ligands. It is reported that the 1,4-diazabutadiene (DAB) can be reduced by $CrCl_2$, forming Cr(III) complexes bearing radical-anion ligands.[24] So far no such Cr(III) BIAN complex and reactivity was reported. Moreover, despite the extensive studies of the complexes based on diimine BIAN ligands, the complexes with monoimine ligands still remain less investigated, although the ligands were reported previously.[25]

In this regard, herein we wish to report the synthesis of radical-anion BIAN Cr(III) complexes by the one-pot reaction of $CrCl_2(THF)_2$ with BIAN ligands. Similar reactions of $CrCl_2(THF)_2$ with monoimine ligands afford dinuclear chromium complexes with NNOO tetradentate ligands via the pinacol cross-coupling reaction.

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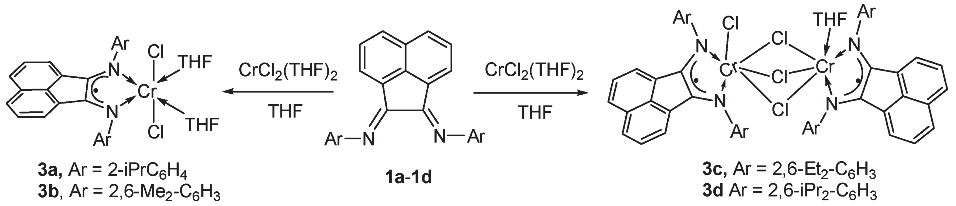
Scheme 1. Synthetic Route for the BIAN Chromium(III) Complexes



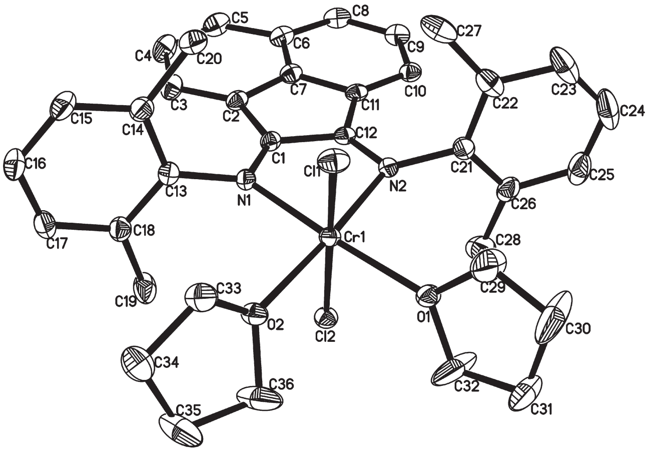


Figure 1. Perspective view of **3b** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)−Cl(1) 2.3255(13), Cr(1)−Cl(2) 2.3346(12), Cr(1)−N(1) 2.013(3), Cr(1)−N(2) 2.025(3), Cr(1)−O(1) 2.110(3), Cr(1)−O(2) 2.124(3), C(1)−N(1) 1.331(5), C(12)−N(2) 1.335(5), C(1)−C(12) 1.419(6); Cl(1)−Cr(1)−Cl2 172.27(5), N(1)−Cr(1)−N(2) 81.96(14), O(1)−Cr(2)−O(2) 91.44(12).

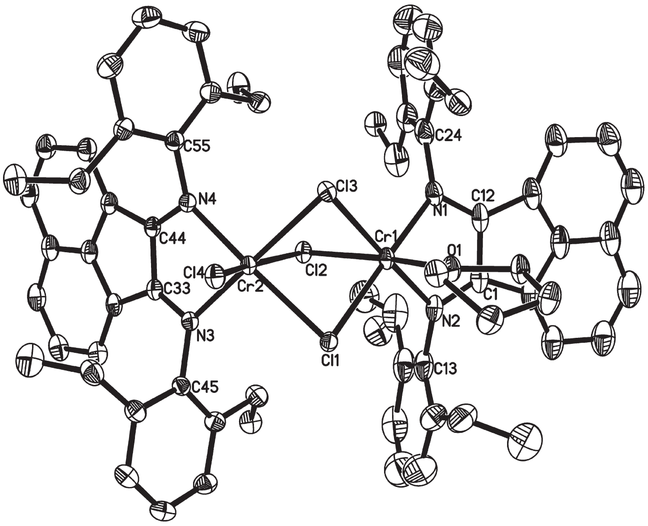


Figure 2. Perspective view of **3c** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)−N(1) 2.006(5), Cr(1)−N(2) 2.001(5), Cr(1)−Cl(1) 2.3978(14), Cr(1)−Cl(2) 2.3682(13), Cr(1)−Cl(3) 2.3789(14), Cr(2)−N(3) 2.000(4), Cr(2)−N(4) 2.002(4), Cr(2)−Cl(2) 2.4645(13), Cr(2)−Cl(3) 2.4184(14), Cr(2)−Cl(4) 2.2902(13), Cr(1)−O(1) 2.075(3); N(1)−Cr(1)−N(2) 82.5(2), N(3)−Cr(2)−N(4) 82.78(16).

The catalytic behaviors of these complexes for diene polymerization were also investigated.

RESULTS AND DISCUSSION

The BIAN ligands were efficiently synthesized according to the literature.[26] Refluxing the acenaphthenequinone with the corresponding substituted aniline in acetonitrile and acetic acid mixed solution afforded the corresponding BIAN ligands in moderate yields. The monoimine ligands were synthesized by treatment of the acenaphthenequinone with substituted aniline in ethanol and catalytic formic acid.[25]

Initial attempts to synthesize the simple Cr(III) complexes with neutral BIAN ligands by stirring the $CrCl_3(THF)_3$ and ligands in various solvents failed. No obvious color change was found, and the ligand was recovered in high yield. Reactions of the BIAN ligands (**1a** and **1b**) with the $CrCl_2(THF)_2$ in THF at room temperature result in immediate changes of color form orange to deep brown. Evaporation of the solvent and recrystallization of the residue in THF/hexane mixed solution afforded **3a** and **3b** as a brown solid in moderate-to-high yield (Scheme 1). No informative NMR spectra of these complexes were obtained due to their paramagnetic nature. Crystals of **3b** suitable for X-ray diffraction determination were grown from THF/hexane solution. The molecular structure is shown in Figure 1 together with the selected bond distances and angles. The crystallographic data is summarized in STable 1 (in the Supporting Information).

X-ray structural analysis reveals that **3b** was a mononuclear complex coordinated with a BIAN ligand, two chlorides, and two THF molecules. The geometries around the chromium atom can be best described as octahedral with the two chlorides arranged in trans positions (bite angle = 172.27(5)°). The two Cr−Cl bond lengths are almost the same length (2.3255(13) and 2.3346(12) Å), which are similar to those of 2.2915(8)−2.3205(7) Å in the NCN-pincer Cr(III) complexes[16] and those of 2.2841(11)−2.3063(12) Å in bis(oxazolinyl)pyridine chromium(III) complexes.[27] The Cr atoms are essentially coplanar with the BIAN coordination plane with the deviation of 0.2892(37) Å. The N−Cr bond lengths of 2.013(3) and 2.025(3) Å are comparable to those of 1.9873(3)−2.158(3) Å in the 2-imino-1,10-phenanthroline chromium complexes[28] and those of 1.981(3)−2.141(3) Å in bis(imino)pyridyl chromium(III) complexes.[29] Careful inspection of the bond lengths within the BIAN moiety is a useful method for evaluating the reduction state of the ligands and the value state of the central chromium atoms.[23] The bond lengths of C(1)−N(1) and C(12)−N(2) in **3b** (1.331(5) and 1.335(5) Å) are very similar to that in the Cr(II) complex with the radical-anion BIAN ligand[23] and lie in the range between that (1.281(5)−1.284(5) Å)

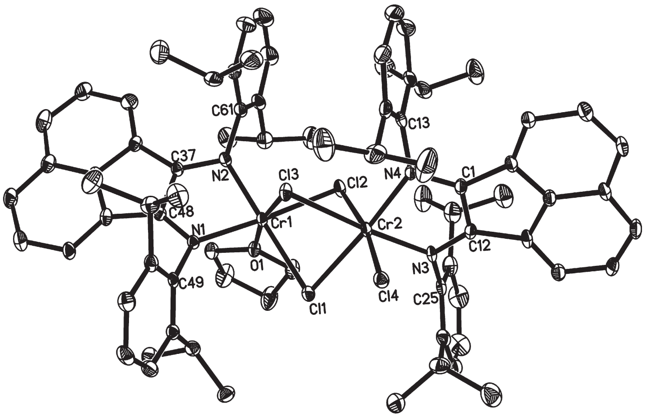


Figure 3. Perspective view of **3d** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)−N(1) 1.999(5), Cr(1)−N(2) 2.009(5), Cr(1)−Cl(1) 2.4002(19), Cr(1)−Cl(2) 2.3768(17), Cr(1)−Cl(3) 2.3392(19), Cr(2)−N(3) 2.016(5), Cr(2)−N(4) 1.990(5), Cr(2)−Cl(2) 2.4288(19), Cr(2)−Cl(3) 2.4298(18), Cr(2)−Cl(4) 2.2946(19), Cr(1)−O(1) 2.092(5); N(1)−Cr(1)−N(2) 82.3(2), N(3)−Cr(2)−N(4) 83.3(2).

for neutral BIAN complexes[30] and that (1.401(6)−1.378(7) Å) for the enediamide complex.[22f] The C(1)−C(12) bond distance of 1.419(6) Å is also similar to that of 1.418(4) Å in the radical-anion BIAN chromium(II) complex.[23] All these structural features strongly suggest that the Ar-BIAN in **3b** was reduced by the Cr(II), forming the radical-anion ligand, and the central chromium atoms should be Cr(III).[24]

Complexes **3c** and **3d** with more steric-demanding ligands were also prepared in a similar procedure as brown powders. Crystals of **3c** and **3d** suitable for an X-ray structure determination were grown from THF solution. The molecular structures of **3c** and **3d** are depicted in Figures 2 and 3 together with the selected bond lengths and angles. **3c** and **3d** are unsymmetrical chlorine-bridging dinuclear complexes with structures similar to that of $[(^{iPr}\mathrm{DBA})\mathrm{Cr}]_2(\mu\text{-Cl})_3(\mathrm{Cl})(\mathrm{THF})$,[24] although the whole structure of **3c** is in a somewhat bent model and **3d** is a little twisted. The bulky ortho substitutes favor the formation of dinuclear complexes completing the coordination sphere with less bulky bridging chlorine atoms. In both complexes, the chromium atoms are six-coordinated and exhibit octahedral geometries. The bond distances of bridging chlorides to Cr(1) of 2.3682(13)−2.3978(14) Å in **3c** and 2.3392(19)−2.4002(19) Å in **3d** are slightly shorter than that to Cr(2) (2.4184(14)−2.4645(13) Å in **3c** and 2.4288(19)−2.4390(19) Å in **3d**). The terminal Cr−C1 bond lengths (2.2902(13) Å in **3c** and 2.2946(19) Å in **3d**) are shorter than exception, but also similar to that of 2.279(1) Å in $[(^{iPr}\mathrm{DBA})\mathrm{Cr}]_2(\mu\text{-Cl})_3(\mathrm{Cl})(\mathrm{THF})$.[24] All the structural characters within the BIAN moieties in **3c** and **3d** are comparable to those in **3b** and also consistent with the radical-anion nature of the ligands.

Intrigued by the successful preparation of the Cr(III) BIAN complexes by the simple one-pot reaction of the BIAN ligands with $\mathrm{CrCl_2(THF)_2}$, we set out to investigate the reaction of $\mathrm{CrCl_2(THF)_2}$ with monoimine ligands. Stirring the mixture of monoimine ligands and $\mathrm{CrCl_2(THF)_2}$ in $\mathrm{CH_2Cl_2}$, evaporation of the solvent, and recrystallization of the residue in $\mathrm{CH_2Cl_2}$/hexane mixed solution afforded complexes **4b** and **4c** in high yields as a green solid. Crystals of **4b** suitable for an X-ray structure determination were grown from a dichloromethane and hexane mixed solution. The molecular structures are shown in Figure 4. The structure reveals that, in the reaction, the two monoimine ligands were reductive dimerized in a piancol cross-coupling mechanism, forming a new dinuclear chromium(III) complex bearing $[\mathrm{NOON}]^{2-}$ tetradentate ligands. Similar pinacol cross-coupling reactions of two carbonyl compounds can be catalyzed by Sm(II),[31a] Al,[31b−d] Mg,[31d] $\mathrm{Zn/ZnCl_2}$,[31e,f] $\mathrm{Zn/InCl_3}$,[31h] and $\mathrm{Al/InCl_3}$[31g] systems. Some $\mathrm{CrCl_2}$-based catalytic systems also show excellent activities in aliphatic carbonyl pinacol cross-coupling reactions.[32] It is well known that the first step of the piancol

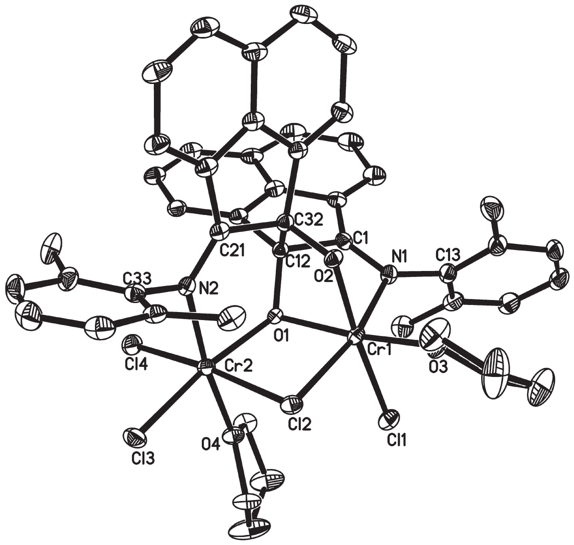


Figure 4. Perspective view of **4b** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. The selected bond lengths (Å) and angles (deg): Cr(1)−Cl(1) 2.3206(18), Cr(1)−Cl(2) 2.3355(17), Cr(1)−O(1) 2.019(4), Cr(1)−O(2) 1.931(4), Cr(1)−N(1) 2.070(5), Cr(1)−O(3) 2.036(4), Cr(2)−Cl(2) 2.3833(17), Cr(2)−Cl(3) 2.3029(18), Cr(2)−Cl(4) 2.2892(18), Cr(2)−O(1) 2.015(4), Cr(2)−N(2) 2.133(5), Cr(2)−O(4) 2.044(4); Cl(1)−Cr(1)−Cl(2) 91.41(6), Cl(3)−Cr(2)−Cl(4) 90.76(7), N(1)−Cr(1)−O(1) 80.71(17), N(2)−Cr(2)−O(1) 88.72(17).

Scheme 2. Pinacol Cross-Coupling Reaction of Monoamine Ligands with $\mathrm{CrCl_2(THF)_2}$

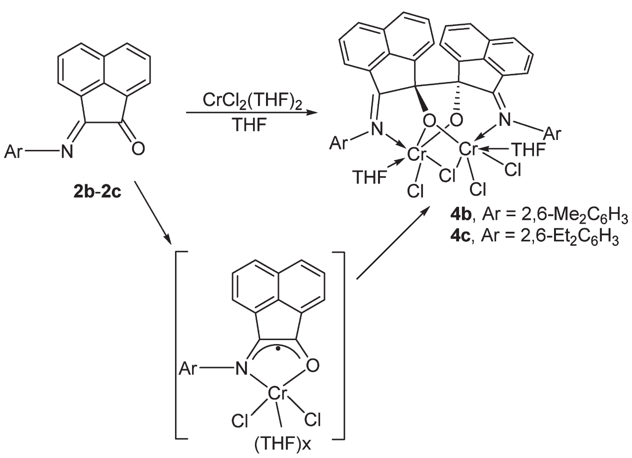


Table 1. Polymerization of Isoprene and Butadiene under Various Conditions[a]

entry	cat	monomer	Tp (°C)	Al/Cr	time (min)	conv (%)	M_n[b] ($\times 10^4$)	PDI	microstructure[c] (%) cis-1,4-	microstructure[c] (%) 3,4- or 1,2-
1	**3a**	IP	25	500	30	95.7	0.86	1.53	56.2	43.8
2	**3b**	IP	25	500	30	73.8	3.04	1.72	68.9	31.1
3	**3c**	IP	25	500	30	77.9	1.86	1.63	73.4	26.6
4	**3d**	IP	25	500	30	82.6	7.65	1.20	80.0	20.0
5	**4b**	IP	25	500	30	60.0	0.71	3.62	79.8	21.2
6	**4c**	IP	25	500	30	63.8	3.41	2.57	79.0	21.0
7	**3d**	IP	25	200	30	48.1	9.84	1.07	81.0	19.0
8	**3d**	IP	25	800	30	88.2	7.83	1.13	76.4	23.6
9	**3d**	IP	25	1000	30	89.6	4.42	1.39	77.6	22.4
10	**3a**	BD	25	500	30	91.7	0.42	2.77	70.4	29.6
11	**3b**	BD	25	500	30	89.5	0.70	2.35	77.9	22.1
12	**3c**	BD	25	500	30	88.8	1.06	1.90	82.9	17.1
13	**3d**	BD	25	500	30	90.2	1.69	1.61	89.3	10.7
14	**4b**	BD	25	500	30	86.3	0.20	1.81	87.0	13.0
15	**4c**	BD	25	500	30	81.7	0.58	1.72	88.5	11.5
16	**3d**	BD	0	500	360	33.4	1.84	1.29	92.1	7.9
17	**3d**	BD	−20	500	360	30.8	1.10	1.15	94.3	5.7
18	**3d**	BD	−40	500	360	24.2	0.85	1.13	95.2	4.8

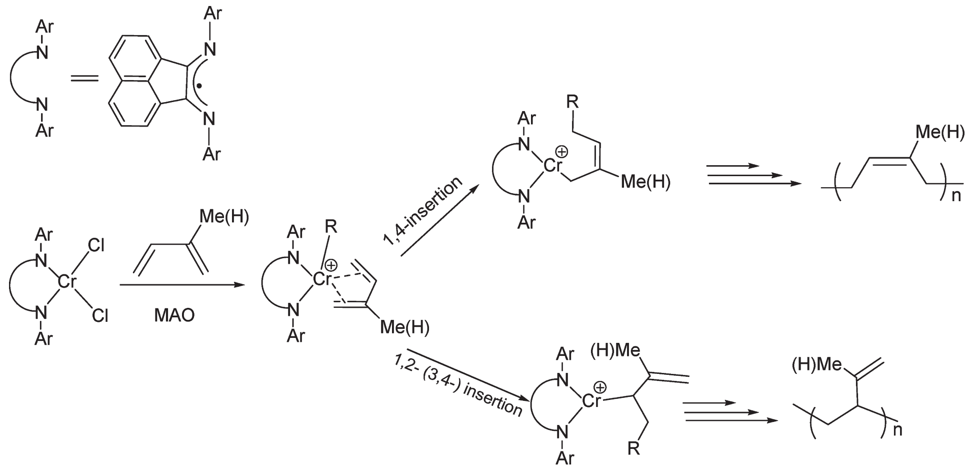
[a] The polymerization reactions: toluene (10 mL), cat (20 μmol based on Cr), isoprene (10 mmol), monomer/Cr = 500. [b] Determined by gel permeation chromatography (GPC) with respect to a polystyrene standard. [c] Determined by NMR spectrum and IR.

cross-coupling reaction is the generation of a radical enolate chromium complex formed via transfer of one electron from Cr(II) to aldehyde or keton.[32,33] In our case, the conjugated frames of the ligand favor the formation of radical species, and we assume that a radical-anion intermediate complex (see Scheme 2) was formed first, which undergoes a fast intermolecular cross-coupling reaction. Similar radical-anion chromium complexes can be stabilized by phenanthrene monoimine ligands. Figure 4 shows that the two anolate oxygen atoms are arranged in a trans position with respect to the two acenaphthene moieties and both chromium atoms are six-coordinated and the geometry around the chromium atoms could be described as a distorted octahedron. The environments around Cr(1) and Cr(2) are almost the same except that the Cr(1) coordinated with an additional terminal anolate oxygen atom, while Cr(2) coordinated with an additional terminal chloride atom instead. The Cr−Cl bond distances of 2.2892(18)−2.3892(18) Å in **4b** are comparable to those in **3c** and **3d**. The C(1)−N(1) and C(21)−N(2) bond lengths of 1.281(7) and 1.303(8) Å are obviously short than that of 1.322(8)−1.342(8) Å in **3c** and **3d** and have double bond character.

BUTADIENE AND ISOPRENE POLYMERIZATION

All the complexes were investigated as catalysts for butadiene and isoprene polymerization. The polymerization data are summarized in Table 1. All the complexes were almost inert in diene polymerization when only AlR_3 was used as cocatalysts. When activated with MAO, these complexes show medium-to-high activities toward isoprene polymerization with varied *cis*-1,4 selectivity at room temperature and the diimine complexes show relatively higher activities than that with **4b** and **4c**. Complex **3a** with one *ortho*-isopropyl substitute at imine groups show the highest activity; a conversion of 95.7% was achieved in 30 min, affording the PIP with only 56.2% *cis*-1,4 selectivity. When those complexes bearing ortho disubstitute ligands (**3b**−**3d**) were used, the bulkiness of ortho substitutes shows a slightly influence on the activities and *cis*-1,4 selectivities, and the conversions and cis-1,4 selectivities gradually increased with the increase of the size of the ortho substitutes (entries 2−4, Table 1). Activated with MAO, the generated cationic metal center lies in an opening environment (the bite angles of the two aryl rings in **3b** are nearly 172.5°), and we think the difference in selectivity may be attributed to the electronic factor rather than the steric factor. It can be seen that the molecular weights of resulting polymers have an essentially increasing tendency with respect to the increase of the number and bulkiness of ortho substitutes (entries 1−4, Table 1). This may be due to the difference in the stabilities of resulting active species during the polymerization. The ortho substitutes may donate the electrons to the metal center and make the active center more stable and able exist for a long time. The tetradentate complexes **4b** and **4c** show moderate activities in isoprene polymerization, affording the PIP with similar *cis*-1,4 selectivity (79.8% and 79.0% in entries 5−6, Table 1). The catalytic activity was also affected by the ratio of Al/Cr used. When **3d** was used as a precatalyst (entries 4 and 7−9, Table 1), the conversion increased with the increasing Al/Cr ratios and an 82.6% conversion was achieved at Al/Cr = 500. A further increase in Al/Cr molar ratios shows no obvious effects on the productivities. Upon activation with MAO, these complexes also show high activities in butadiene polymerization at room temperature. It is worth to note that, unlike other chromium complexes that afforded the 1,2-enriched polymer, these complexes show moderate-to-high *cis*-1,4 selectivity in butadiene polymerization. The diimine complexes **3a**−**3d** show similar activities, and an 88.8−91.7% conversion was achieved, whereas with the increase of the number and size of the ortho substitutes, the *cis*-1,4 selectivtieis gradually increased from 70.4% to 89.3%, accompanying with the gradual increase of the

Scheme 3. Proposed Mechanism for Diene Polymerization by BIAN Cr(III) Complexes



molecular weight (entries 10−13, Table 1). **4b** and **4c** show similar activities and selectivities. It is worth to note that the selectivity is influenced by the polymerization temperature and the *cis*-1,4 selectivity gradually increased from 89.3% at 25 °C to 95.2% at −40 °C.

On the basis of the data mentioned above, we assumed a cationic mechanism (Scheme 3). The activation of the BIAN chromium complexes with MAO affords a cationic metal center. The opening environment around the cationic metal center favors the coordination of diene in a cis η^4 manner and affords the *cis*-1,4-enriched polymer.

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 $CDCl_3$ solution for ligands and polymers. The molecular weight and molecular weight distribution of the polymers were measured by a TOSOH HLC 8220 GPC at 40 °C using THF as the eluent against polystyrene standards. The ligands were synthesized according to the literature. Acenaphthenequinone, 2,6-dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, and 2-isopropylaniline were bought from Aldrich Chemical Co. and used without further purification. (2,-^{i}PrC$_6$H$_4$-BIAN) (**1a**),[24] (2,6-Me$_2$C$_6$H$_3$-BIAN) (**1b**),[24] (2,6-^{i}Pr$_2$C$_6$H$_3$-BIAN) (**1d**),[24] and *N*-(2,6-dimethylphenylimino)-acenaphthenone (**2b**)[25a] were synthesized according to the literature.

*1,2-Bis[(2,6-diethylphenyl)imino]-acenaphthene (2,6-Et$_2$C$_6$H$_3$-BIAN) (**1c**).* 1,2-Bis[(2,6-diethylphenyl)imino]-acenaphthene was synthesized with a similar procedure to that for 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene. Acenaphthenequinone (1.35 g, 7.4 mmol) in 65 mL of acetonitrile was heated under reflux for 30 min, and then 12 mL of acetic acid was added and heating was continued until the acenaphthenequinone had completely dissolved. To this hot solution, 2.39 g (16 mmol) of 2,6-diethylaniline was added directly, and the solution was heated under reflux for a further 1.5 h. It was then cooled to room temperature, and the solid was filtered off to give a yellow product that was washed with hexane and air-dried. Yield: 2.73 g (83%). Anal. Calcd for $C_{32}H_{32}N_2$ (%): C, 86.44; H, 7.25; N, 6.30. Found: C, 86.45; H, 7.29; N, 6.36. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.13 (t, J_{H-H} = 9.0 Hz, 12H, CH_2CH_3), 2.49 (m, 4H, CH_2CH_3), 2.60 (m, 4H, CH_2CH_3), 6.71 (d, 2H), 7.22 (m, 6H), 7.37 (t, 2H), 7.87 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 8.74, 19.58, 117.77, 118.81, 121.28, 122.94, 123.68, 124.41, 125.55, 125.86, 135.46, 143.43, 155.61 ppm.

*((2,6-Diethylphenyl)imino)-acenaphthenone (**2c**).* ((2,6-Diethylphenyl)imino)-acenaphthenone was synthesized with a similar procedure to that for ((2,6-diisopropylphenyl)imino)-acenaphthenone. Acenaphthenequinone (3.2 g, 18 mmol) and Na_2SO_4 (15 g) were stirred at 45 °C in 500 mL of methanol. 2,6-Diethylaniline (1.94 g, 16 mmol) and formic acid (0.60 mL) in 100 mL of methanol were added dropwise to the acenaphhenequinone solution for 3 h. After 10 h, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (20% ethyl acetate/hexane, silica gel) to afford 3.9 g of a red-orange powder (yield: 78%). Anal. Calcd for $C_{22}H_{19}NO$(%): C, 84.31; H, 6.11; N, 4.47. Found: C, 84.27; H, 6.08; N, 4.40. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.06 (t, J_{H-H} = 9.0 Hz, 12H, CH_2CH_3), 2.35 (m, 4H, CH_2CH_3), 2.48 (m, 4H, CH_2CH_3), 6.68 (d, 1H), 7.21 (s, 3H), 7.43 (t, J_{H-H} = 6.0 Hz, 1H), 7.84 (t, J_{H-H} = 9.0 Hz, 1H), 8.01 (d, J_{H-H} = 6.0 Hz, 1H), 8.19 (d, J_{H-H} = 3.0 Hz, 1H), 8.21 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 8.71, 19.21, 116.82, 117.65, 119.42, 121.08, 122.43, 122.99, 123.09, 124.16, 125.14, 125.53, 125.70, 126.93, 137.67, 142.43, 155.00, 184.25 ppm.

*(2-^{i}PrC$_6$H$_4$-BIAN)CrCl$_2$(THF)$_2$ (**3a**).* A mixture of **1a** (0.416 g, 1.00 mmol) and $CrCl_2(THF)_2$ (0.266 g, 1.00 mmol) in 20 mL of THF was stirred for 6 h at 25 °C under a nitrogen atmosphere. The solution was concentrated to 6 mL to give a brown powder, from which the mother liquor was decanted, and the product was washed with 5 mL of ether and dried in vacuum. The product was isolated as a brown solid (0.561 g, 82% yield). Anal. Calcd for $C_{38}H_{44}Cl_2CrN_2O_2$ (%): C, 66.76; H, 6.49; N, 4.10. Found: C, 66.76; H, 6.52; N, 4.13. IR(KBr): ν (cm^{-1}) 3233 w, 3053 w, 2963 s, 2853 w, 1727 w, 1676 w, 1625 m, 1567 m, 1520 w, 1470 s, 1424 w, 1361 w, 1180 w, 1141 w, 1111 w, 1045 m, 1000 w, 930 w, 859 w, 807 w, 769 s, 678 w, 588 w, 569 w, 537 w.

*(2,6-Me$_2$C$_6$H$_3$-BIAN)CrCl$_2$(THF)$_2$ (**3b**).* The synthesis of **3b** was carried out according to that of complex **3a**, using 0.389 g of ligand **1b** (1.00 mmol) and $CrCl_2(THF)_2$ (0.266 g, 1.00 mmol). Yield: 0.518 g (79%) of a brown powder. Crystals of **3b** suitable for X-ray structural determination were grown in THF/hexane mixed solution. Anal. Calcd for $C_{36}H_{40}Cl_2CrN_2O_2$ (%): C, 65.95; H, 6.15; N, 4.27. Found: C, 65.87; H, 6.10; N, 4.25. IR(KBr): ν (cm^{-1}) 3387 w, 3059 w, 2963 s, 2879 w, 2821 w, 1618 m, 1579 s, 1476 s, 1354 w, 1290 m, 1026 w, 962 w, 897 w, 827 w, 769 s, 665 w, 608 w.

*(2,6-Et$_2$C$_6$H$_3$-BIAN)CrCl(μ-Cl)$_3$Cr(2,6-Et$_2$C$_6$H$_3$-BIAN)(THF) (**3c**).* The synthesis of **3c** was carried out according to that of complex **3a**, using ligand **1c** (0.444 g, 1.00 mmol) and CrCl$_2$(THF)$_2$ (0.266 g, 1.00 mmol). Yield: 0.459 g (76%) of a brown powder. Crystals of **3c** suitable for X-ray structural determination were grown in THF/hexane mixed solution. Anal. Calcd for $C_{68}H_{72}Cl_4Cr_2N_4O$ (%): C, 67.66; H, 6.01; N, 4.64. Found: C, 67.59; H, 5.98; N, 4.57. IR(KBr): ν (cm^{-1}) 3291 w, 3053 w, 2963 s, 2918 m, 2867 m, 1683 w, 1643 w, 1618 m, 1580 s, 1457 m, 1431 m, 1361 w, 1290 m, 1232 w, 1180 w, 1129 w, 1051 w, 948 w, 878 w, 839 m, 769 s, 743 m, 547 w.

*(2,6-^{i}Pr$_2$C$_6$H$_3$-BIAN)CrCl(μ-Cl)$_3$Cr(2,6-^{i}Pr$_2$C$_6$H$_3$-BIAN)(THF) (**3d**).* The synthesis of **3d** was carried out according to that of complex **3a**, using ligand **1d** (0.501 g, 1.00 mmol) and CrCl$_2$(THF)$_2$ (0.266 g, 1.00 mmol). Yield: 0.574 g (87%) of a brown powder. Crystals of **3d** suitable for X-ray structural determination were grown in THF/hexane mixed solution. Anal. Calcd for $C_{76}H_{88}Cl_4Cr_2N_4O$ (%): C, 69.19; H, 6.72; N, 4.25. Found: C, 69.21; H, 6.81; N, 4.31. IR(KBr): ν (cm^{-1}) 3060 w, 2963 s, 2867 m, 1734 w, 1618 m, 1573 s, 1451 s, 1424 m, 1354 w, 1322 w, 1290 m, 1245 w, 1180 w, 1129 w, 1038 w, 935 w, 832 m, 814 m, 788 m, 756 s, 600 w, 537 w.

*2,6-Me$_2$C$_6$H$_3$-BIAO(κ^3N,O,O′-CrClTHF)(μ-Cl)(μ-O)(κ^2N′,O-CrCl$_2$THF) (**4b**).* A mixture of **2b** (0.285 g, 1.0 mmol) and CrCl$_2$(THF)$_2$ (0.266 g, 1.0 mmol) in 20 mL of CH$_2$Cl$_2$ was stirred for 6 h at 25 °C under a nitrogen atmosphere and concentrated to 5 mL to give a pale green powder, from which the mother liquor was decanted, and the product was washed with 2 mL of hexane and dried in vacuum. The product was isolated as a pale green solid (0.409 g, 85% yield). Crystals of **4b** suitable for X-ray structural determination were grown in CH$_2$Cl$_2$ /hexane mixed solution. Anal. Calcd for $C_{48}H_{48}Cl_4Cr_2N_2O_4$(%): C, 59.88; H, 5.03; N, 2.91. Found: C, 59.86; H, 5.00; N, 2.87. IR(KBr): ν (cm^{-1}) 3240 w, 3066 w, 2970 s, 2873 m, 1721 w, 1637 s, 1592 m, 1464 m, 1424 w, 1341 w, 1270 w, 1187 w, 1045 w, 955 w, 904 w, 827 w, 781 s, 620 w.

*2,6-Et$_2$C$_6$H$_3$-BIAO(κ^3N,O,O′-CrClTHF)(μ-Cl)(μ-O)(κ^2N′,O-CrCl$_2$THF) (**4c**).* The synthesis of **4c** was carried out according to that of complex **4b**, using ligand **2c** (0.313 g, 1.00 mmol) and CrCl$_2$(THF)$_2$ (0.266 g, 1.00 mmol). Yield: 0.407 g (80%) of a pale green solid. Crystals of **4c** suitable for X-ray structural determination were grown in CH$_2$Cl$_2$ / hexane mixed solution. Anal. Calcd for $C_{52}H_{56}Cl_4Cr_2N_2O_4$ (%): C, 61.30; H, 5.54; N, 2.75. Found: C, 61.36; H, 5.59; N, 2.82. IR(KBr): ν (cm^{-1}) 3265 w, 2969 s, 2867 m, 1727 w, 1637 s, 1592 s, 1451 m, 1335 w, 1277 w, 1187 m, 1038 s, 1006 s, 852 s, 769 m, 672 w, 614 w, 543 w, 504 w, 453 w.

General Procedure for Butadiene and Isoprene Polymerization. In a typical polymerization experiment, toluene (10 mL), isoprene or butadiene (10 mmol), and 20 mmol MAO were added into a 25 mL flask. Complex **3a** (20 μmol) was then 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, which were filtered and dried under vacuum at 40 °C for 24 h.

X-ray Crystal Structural Determination. The crystals were mounted on a glass fiber using the oil drop. Data obtained with the ω-2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo−Kα radiation (λ = 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.[34] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. The molecular structures of **3a** and **4c** were also confirmed by the X-ray diffraction analysis and were not depicted in the paper due to unsolvable disorder in **3a** and a large R_{int} in **4c**. The large solvent accessible VOID(S) was found in **3d** due to the severe disorder of the uncoordinated THF molecules.

■ CONCLUSIONS

In summary, we have reported the synthesis of the radical-anion Cr(III) complexes by reducing the BIAN ligands with CrCl$_2$(THF)$_2$. The monoimine ligands undergo a pinacol cross-coupling reaction, affording the tetradentate dinuclear Cr(III) complexes. These Cr(III) complexes show high activities in isoprene and butadiene polymerization, affording the *cis*-1,4-enriched polymer.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic data and refinements for complexes **3b**−**3d** and **4b** in CIF format, summary of crystallographic data, and typical ^{13}C NMR spectra of polybutadiene and polyisoprene. This material is available free of charge via the Internet at http://pubs.acs.org.

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