Stereospecific Polymerizations of Conjugated Dienes by Single Site Iron Complexes Having Chelating N,N,N-Donor Ligands

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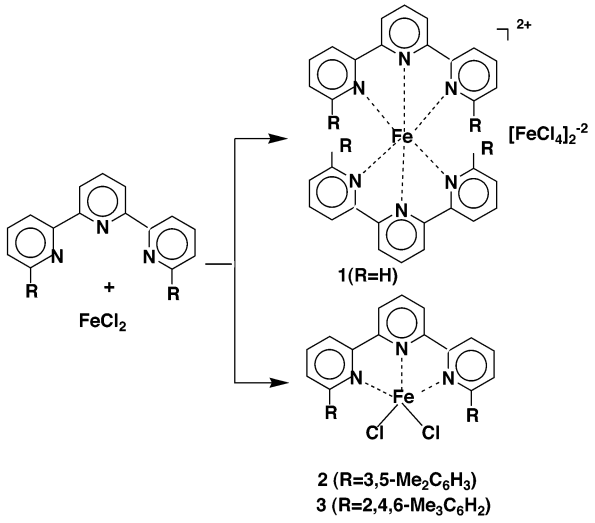
ABSTRACT: Iron−terpyridine complexes, [Fe(terpyridine)$_2$](FeCl$_4$)$_2$ (**1**), FeCl$_3$(terpyridine) (**4**), and FeCl$_3$-(4,4′,4″-tri-*tert*-butylterpyridine) (**5**), were found to display high catalytic activities for 1,2/3,4-polymerizations of isoprene and trans-1,4-polymerization of 1,3-butadiene in the presence of MMAO (modified methylalumoxane), whereas FeCl$_2$(6,6″-diarylterpyridine) complexes **2** and **3** exhibit no catalysis for polymerizations of these two monomers even in the presence of MMAO. The N,N,O-ligated *N*-(2-pyridyl)-methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine complex (**6**) of FeCl$_2$ and the corresponding *N*-(2-pyridyl)-2-oxy-3,5-di-*tert*-butylbenzaldimine/FeCl (**7**) revealed more efficient catalysis for polymerization of isoprene and 1,3-butadiene. In sharp contrast to these N,N,N-donor or N,N,O-donor ligated complexes, N,N-ligated FeCl$_2$(sparteine) complex **8** shows much lower catalytic activities, although the stereospecifity is much higher.

Introduction

There has been recent interest in the use of soluble transition metal catalysts such as CpTiCl$_3$/MAO,[1−3] CpTiCl$_2$/MAO,[4] CpTiCl$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$/AliBu$_3$,[5] Ti(OiPr)$_4$/MAO,[6] Ti(CH$_2$Ph)$_4$/MAO,[7] Ni(acac)$_2$/MAO,[8] Co(acac)$_2$/MAO,[9] and Ni(oct)$_2$/AlF$_3$/AlEt$_3$[10] for 1,4-polymerizations of isoprene and 1,3-butadiene to obtain high molecular weight polymers with low polydispersities as efficient low-cost materials for improved synthetic rubber. 1,2-Poly(1,3-butadiene) and 3,4-poly(isoprene) have also been prepared using homogeneous catalysts like V(acac)$_3$/AlEt$_3$[11] and Cr(acac)$_3$/MAO[12] to use as plastic rollers for printing of polymer films, seals, and children's toys. However, the use of other metal complexes is scarcely known.[13,14] More recently, Brookhart and Gibson et al. reported the excellent catalysis of N,N,N-donor (pyridinediimine ligand)/FeCl$_2$ complexes activated by MAO for polymerizations of ethylene and olefins.[15] However, these initiators are completely inert toward the polymerizations of conjugated dienes. The iron catalyst systems effective for polymerizations of conjugated dienes reported so far are limited only to Fe(acac)$_3$/AlisoBu$_3$/electron donor[16] and Fe(acac)$_3$/AlEt$_3$/phenyl-2-pyridylacetonitrile.[17] We have explored here to find more efficient catalysis using terpyridine complexes of FeCl$_2$ or FeCl$_3$ for polymerizations of conjugated dienes. The large number of possible variations in this catalyst system allows for more specifically designed catalysts, possibly selective for the optimized polymerizations of desired conjugated dienes or the production of their copolymers. As a result, we could find the efficient catalysis using terpyridine complexes of FeCl$_2$ and FeCl$_3$ for homopolymerizations of isoprene and 1,3-butadiene as well as the copolymerizations of isoprene with 1,3-butadiene. More recently, Fujita et al. found that N,O-ligated bis(phenoxyimine) complexes of MCl$_2$ (M = Ti, Zr, Hf) exhibit extremely high catalytic activity for the polymerizations of ethylene.[18] Therefore, we also explored the catalysis of the N,N,O-ligated [*N*-(2-pyridyl)methyl-2-oxy-benzaldimine]/FeCl$_2$ complex for polymerization of conjugated dienes. To compare with the catalyses of N,N,N- and N,N,O-ligated complexes, that of the N,N-ligated sparteine complex of FeCl$_2$ was also investigated.

Scheme 1



Results and Discussion

Preparation of Iron Complexes Having Chelating N-Donor Ligands. A series of terpyridine−iron complexes **1**−**5** were prepared by the stoichiometric reactions of anhydrous FeCl$_2$ (Scheme 1) or FeCl$_3$ (Scheme 2) with the corresponding terpyridine ligands in high yields. A stoichiometric reaction of *N*-(2-pyridyl)-methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine with FeCl$_2$ in THF at room temperature produces a desired

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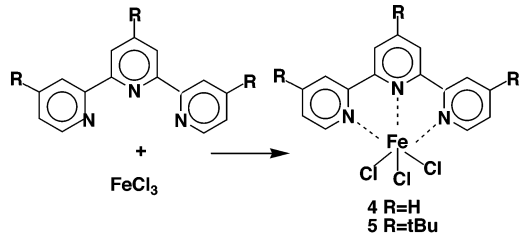
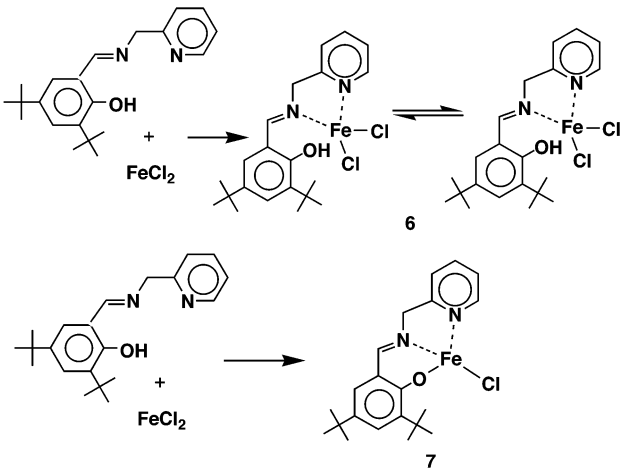
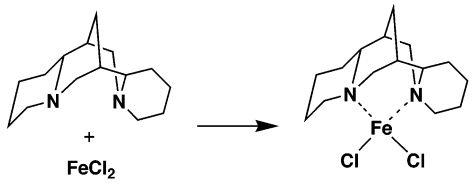
Scheme 2



Scheme 3



Scheme 4



neutral complex **6** in high yield (90.0%) and the reaction of Li salt of the corresponding *N*-(2-pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine with $FeCl_2$ in THF gave *N*-(2-pyridyl)methyl-2-oxy-3,5-di-*tert*-butylbenzaldimine/FeCl complex (**7**) in a moderate yield as a black powder (Scheme 3). To compare the catalyses of N,N,N-donated terpyridine complexes **1**−**5** and N,N,O-donated pyridylmethyl-2-oxy-benzaldimine complexes **6** and **7**, we also prepared a sparteine complex of iron, $FeCl_2$(sparteine) (**8**), from a reaction of $FeCl_2$ and (*S*)-(−)-sparteine (Scheme 4).

Homopolymerizations of Isoprene and 1,3-Butadiene. Since Brookhart et al. found that the $FeCl_2$ complex of a N,N,N-donor ligand (pyridine derivative containing diimine group) exhibits excellent catalysis with the assistance of MAO toward the polymerization of ethylene,[15] we have examined the catalysis of analogous N,N,N-donor complexes of $FeCl_2$ or $FeCl_3$ **1**−**5**, N,N,O-donor complexes **6** and **7**, and N,N-ligated $FeCl_2$ complex **8** toward the polymerization of olefins. However, we found only very low activities of **2** and **3**/MMAO systems for ethylene polymerization (90 gPE mol^{-1} atm^{-1} h^{-1} for **2** and 70 gPE mol^{-1} atm^{-1} h^{-1} for **3**), and all the other complexes were completely inactive toward the polymerizations of ethylene, 1-pentene, and 1,5-hexadiene as well as polar monomers such as methyl methacrylate and acrylonitrile even in the presence of MAO or MMAO. In sharp contrast to these results, the catalysts **1**, **4**, **5** containing terpyridine and **6**, **7** containing pyridylbenzaldimine supporting groups demonstrated the potential for controlling the activity for polymerizations of isoprene and 1,3-butadiene and enhancing the stability of catalyst system. The results are summarized in Tables 1 and 2. Both MMAO and complexes **1**−**8** exhibited no catalysis by themselves toward the polymerization of isoprene and 1,3-butadiene. Good catalysis emerged for the first time by mixing the complexes **1** and **4**−**8** with MMAO in a molar ratio of 1/100 for the polymerization of isoprene. However, complexes **2** and **3** lack the catalysis completely even in the presence of MMAO in a molar ratio of 1/20−1/1000. This is presumably due to the saturation of the coordination sites for initiating the diene polymerization because of the blocking of the metal center by the surrounding N-donors as well as aromatic groups substituted at 6- and 6″-positions. Therefore, 6- and 6″-positions should be opened for gaining the catalytic activity.

Complex **1** exhibits excellent catalysis for isoprene at 25 °C to give high molecular weight polymers with low polydispersities ranging from 1.31 to 2.74, which comprises of a mixture of 1,2-, 3,4-, and *cis*-1,4-poly(isoprene) in a ratio of 36:50:14 (Table 1).

Complex **4** also exhibits good catalysis leading to high molecular weight polymers composed of 1,2-, 3,4-, and *cis*-1,4-poly(isoprene) in a ratio of 27:61:12. Thus, terpyridine/$FeCl_n$ complexes reveal the high catalytic activity for isoprene affording 1,2- and 3,4-rich poly(isoprene). A more pronounced tendency was observed when we used complex **5**, the solubility of which is higher than that of complex **4**. At 0−25 °C, the relative amount of 3,4-poly(isoprene) reached >82%. In addition, the 4,4′,4″-tri-*tert*-butylterpyridine complex **5** exhibited a higher activity than the terpyridine complexes **1** and **4** (Figure 1). The activities of **1** and **4** can be roughly estimated to be 6 kg mol^{-1} h^{-1} and that of **5** to be 14 kg mol^{-1} h^{-1} at the early stage of the polymerization, although the reaction conditions had not been optimized. In contrast to the terpyridine complexes, the selectivities using **6** and **7** decreased; i.e., the relative ratio of *cis*-1,4-poly(isoprene) increased to 25−37%, while 3,4-polymer decreased to 46−53%. More stereospecific polymerization was realized using complex **8**, which demonstrated 3,4-polymerization of isoprene in 99% selectivity, although the activity was rather low.

Complexes **1** and **4**−**7** also showed excellent catalysis for polymerizations of 1,3-butadiene at 25 °C (Table 2). Yields were almost quantitative when we used **1** and **4**−**7** as initiators. The polymerization with **1** gives rise to the formation of a mixture of *cis*-1,4-, *trans*-1,4-, and 1,2-poly(butadiene) in a ratio of 20:51:29, while complex **4** produces predominantly the *trans*-1,4-rich polymer, although the molecular weight distributions are rather broad (M_w/M_n = 3.09−3.75). Complex **5** gave polymers with very high molecular weights (M_n = (62.1−96.5) × 10^4) and low polydispersities, but the resulting polymers are composed of a mixture, *cis*-1,4-, *trans*-1,4-, and 1,2-poly(butadiene) in a ratio of 28:20:52. Complexes **6** and **7** also show the high catalytic activity. In these cases, the formation of 1,2-polymer decreased to 38%, and that of *trans*-1,4-polymer increased to 37−39% from those obtained by **5**. Complexes **2** and **3** again show no catalysis, and complex **8** exhibits only a small catalytic activity.

Random Copolymerizations of Isoprene with 1,3-Butadiene. Since complexes **4** and **5** exhibit high catalytic activity toward polymerizations of both iso-

Table 1. Homopolymerizations of Isoprene with Complexes 1−8/MMAO[a]

							microstructure (%)[c]			
complex	time (h)	temp (°C)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n	T_g (°C)[b]	*cis*-1,4	*trans*-1,4	1,2	3,4
1	12	−78	0							
	12	0	99	77.7	2.39	−1.7	7	0	31	52
	12	25	99	63.2	1.72	1.6	14	0	36	50
	12	60	24	14.9	1.97	−1.0	17	0	7	76
2	12	25	0							
3	12	25	0							
4	12	−20	37	75.8	1.98	−2.8	17	0	5	78
	12	0	99	185.6	1.31	−0.6	12	0	27	61
	12	25	99	146.8	1.41	3.1	12	0	27	61
5	6	0	99	82.6	1.76	9.8	10	0	5	85
	3	25	99	47.0	2.08	3.4	15	3	0	82
6	3	25	99	35.8	2.13	−16.8	25	0	22	53
7	3	25	99	56.3	2.93	−27.1	37	0	17	46
8	12	−20	9	247.9	1.77		0	0	1	99
	12	0	7	278.5	1.52		0	0	1	99
	12	25	0							
$FeCl_2$	12	25	0							

[a] MMAO/initiator = 100 mol/mol, solvent, toluene, [solv]/[monomer] = 10 weight/weight. [b] Determined by DSC. [c] Determined by ^1H NMR.

Table 2. Homopolymerizations of 1,3-Butadiene with Complexes 1−8/MMAO[a]

							microstructure(%)[c]		
complex	time (h)	temp (°C)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n	T_g (°C)[b]	*cis*-1,4	*trans*-1,4	1,2
1	6	0	99	28.5	1.47	−53.4	29	30	41
	6	25	99	1.2	1.25	−61.1	20	51	29
	6	60	8	1.3	7.95	−49.6	25	68	7
2	12	25	0						
3	12	25	0						
4	4	−20	99	4.2	3.75	−49.8	0	94	6
	4	0	99	1.0	3.09	−55.5	1	93	6
	4	25	99	0.5	1.1	−50.0	0	96	4
5	3	0	99	96.5	1.55	−40.0	28	20	52
	3	25	99	62.1	1.74	−46.8	31	23	46
6	1	25	99	8.0	1.72	−59.1	26	39	38
7	3	25	99	75.9	2.87	−56.4	25	37	38
8	12	−20	2	101.5	2.11	-	0	75	25
	12	0	0						
$FeCl_2$	12	25	0						

[a] MMAO/initiator = 100 mol/mol, solvent, toluene, [solv]/[monomer] = 30 weight/weight. [b] Determined by DSC. [c] Determined by ^1H NMR.

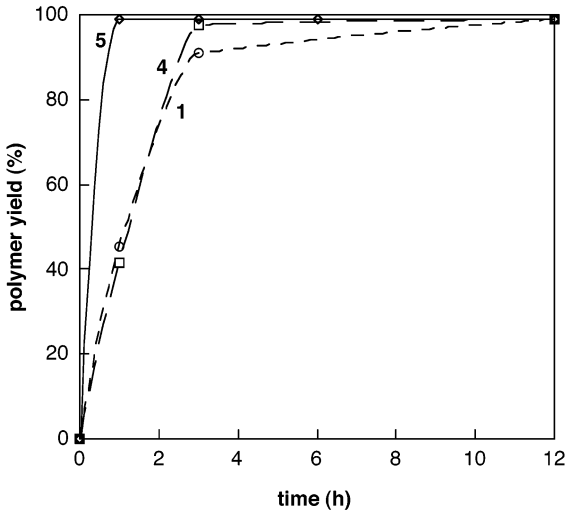


Figure 1. Time dependence of the polymer yields in the polymerization of isoprene by terpyridine−iron complexes **1**, **4**, and **5**/MMAO systems. Conditions: [Al]/[Fe] = 100, $[isoprene]_0/[Fe] = 200$, in toluene, at 25 °C.

prene and 1,3-butadiene, we explored the *random* copolymerizations of isoprene with butadiene to find new materials. These initiators are inert to polymerizations of norbornene, 1,3-cyclopentadiene, and dicyclopentadiene. The results of copolymerization of isoprene with 1,3-butadiene are summarized in Table 3. The random copolymer containing isoprene and 1,3-butadiene in a ratio of 59/41 (obtained with **5**) shows a unimodal pattern in GPC spectrum. Such a pattern was also observed for homopoly(isoprene) and homopoly(1,3-butadiene), as illustrated in Figure 2. Although the feed ratio of isoprene to 1,3-butadiene was a 1/1 molar ratio, complex **4** performed the preferential incorporation of 1,3-butadiene (89−88%) into the copolymer, whereas complex **5** prefers isoprene rather than 1,3-butadiene due to the increased electronegativity on the ligand by the inductive effect of *t*-Bu groups. Thus, the subtle difference of substituent greatly affects the constitution of the resulting copolymers. The relative ratio of the 3,4-poly(isoprene) unit in the copolymer decreased from that in a homopolymer, and the *cis*-1,4-poly(isoprene) unit increased to ca. 40 mol %. However, the constitution of poly(1,3-butadiene) does not change significantly. In the case of **4**, a remarkable decrease of molecular weight of copolymers was observed when compared with the molecular weight of homopoly(isoprene). This result agrees well that complex **4** gives rise to the formation of relatively low molecular weight poly(1,3-butadiene). The formation of 98 mol % of *trans*-1,4-poly(1,3-butadiene) unit in the copolymer by **4** is nearly comparable to that obtained for a homopoly(1,3-butadiene).

Table 3. Random Copolymerizations of Isoprene with Butadiene[a]

						microstructure (%)						
						BD unit			IP unit			
initiator	time (h)	yield (%)	$M_n \times 10^4$	M_w/M_n	isoprene content (mol %)	*cis*-1,4	*trans*-1,4	1,2	*cis*-1,4	*trans*-1,4	1,2	3,4
4	3	8.0	0.16	1.76	12	1	98	1	38	0	0	62
	6	8.1	0.18	1.81	11	1	98	1	37	0	0	63
5	1	78.7	5.3	2.51	63	1	54	45	30	0	13	57
	3	99.6	4.2	1.51	59	1	76	23	46	0	14	40

[a] Conditions, [Al]/[Fe] = 100 mol/mol, [Fe]/[idsoprene]/[butadiene] = 1/100/100 mol/mol/mol, temperature, 25 °C, 10 mL of toluene, [solvent]/[monomer] = 5 vol/vol.

Table 4. Time Dependence of Random Copolymerizations of Isoprene with Butadiene with 5[a]

						microstructure (%)						
						BD unit			IP unit			
IP/BD mol/mol	time (h)	yield (%)	$M_n \times 10^4$	M_w/M_n	isoprene content (mol %)	*cis*-1,4	*trans*-1,4	1,2	*cis*-1,4	*trans*-1,4	1,2	3,4
75/25	1	51.3	2.8	2.56	81	0	79	21	22	0	30	48
	3	99.5	6.0	1.68	77	0	74	26	23	0	27	50
25/75	1	68.3	2.8	2.13	25	0	70	30	35	0	13	52
	3	99.6	3.8	2.25	24	0	73	27	37	0	12	51

[a] Conditions: [Al]/[Fe] = 100 mol/mol, [Fe]/[monmer] = 1/200 mol/mol, temperature, 25 °C, 10 mL of toluene, [solvent]/[monomer] = 5 vol/vol.

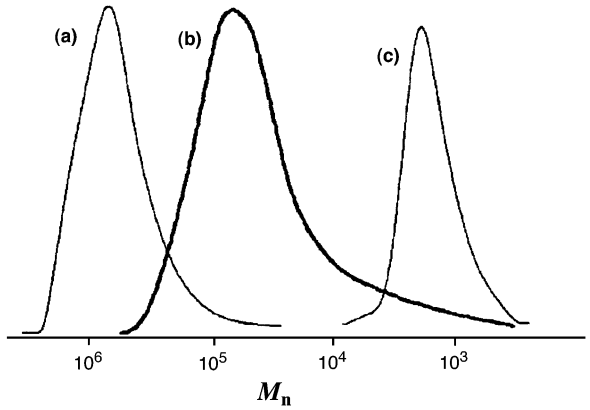


Figure 2. GPC profiles of (a) poly(isoprene) ($M_n = 75.8 \times 10^4$), (c) poly(1,3-butadiene) ($M_n = 0.46 \times 10^4$) obtained with **4** and (b) poly(isoprene-*co*-1,3-butadiene) ($M_n = 4.2 \times 10^4$) obtained with **5**.

As a change of feed ratio between isoprene to 1,3-butadiene from 75/25 to 25/75 molar ratio, the resulting copolymers assume the 77/23−81/19 to 25/75−24/76 ratio. The change of feed ratio does not bring about the significant change of relative ratio of microstructures. Yields increases by the elapse of reaction time (Table 4).

In the case of random copolymerizations using **6** and **7**, resulting polymers always show bimodal pattern. For example, random copolymerization of isoprene and 1,3-butadiene by **6** in the 1:1 ratio at 0 °C gave M_n of 221.5 and 22.1 in a ratio of 13/87 mol/mol. Therefore, we cannot conclude the occurrence of random copolymerizations in these cases.

Mechanical Properties of Resulting Isoprene/1,3-Butdiene Random Copolymers. The mechanical properties of resulting copolymers were measured to find a characteristic feature of the polymer. As a result, homopoly(1,3-butadiene) and 1,3-butadiene copolymers containing more than 75% of poly(1,3-butadiene) unit exhibit very fragile and brittle properties, so that we cannot determine their mechanical properties in detail. In sharp contrast to these materials, homopoly(isoprene) and copolymers containing more than 50% of poly(isoprene) unit show higher tensile strength, higher tensile modulus, and good elongation, as summarized in Table 5. Especially, the copolymer containing 77/23 isoprene/1,3-butadiene molar ratio exhibits high tensile strength and high tensile modulus, although elongation decreased significantly from that of homopoly(isoprene).

Table 5. Mechanical Properties of Copolymer Films Composed of Isoprene and Butadiene[a]

IP/BD ratio	tensile strength (MPa)	tensile modulus (MPa)	elongation (%)
100/0	1.7	n.d.	3035
77/23	4.9	1.2	278
54/46	0.6	n.d.	161

[a] Obtained by complex **5**/MMAO; determined by tensile testing machine.

Conclusion

A series of iron−terpyridine complexes, [Fe(terpyridine)$_2$](FeCl$_4$)$_2$ (**1**), FeCl$_3$(terpyridine) (**4**), and FeCl$_3$(4,4′,4″-*t*-Bu$_3$-terpyridine) (**5**), are highly active for 1,2- and 3,4-polymerizations of isoprene and *trans*-1,4-polymerization of 1,3-butadiene in the presence of MMAO at 25 °C, while FeCl$_2$[6,6″-bis(aryl)terpyridine] **2** and **3** are completely inert toward the polymerizations of isoprene and 1,3-butadiene. The pyridyloxybenzaldimine complexes of FeCl$_2$ **6** and **7** have excellent catalytic activity for polymerizations of isoprene and 1,3-butadiene, although the resulting polymers exhbit a mixture of 1,2- (or 3,4-) and 1,4-polymers. The activity of FeCl$_2$(sparteine) (**8**) is lower than those of **1** and **4**−**7**, but the stereospecificity to conduct the 3,4-polymerization of isoprene is much higher.

Experimental Section

General Procedures. All the operations were performed under argon with standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA-400 spectrometer, and chemical shifts were calibrated with the residual protons ($\delta = 7.26$ ppm) and the carbons ($\delta = 77$ ppm) in CDCl$_3$. The average molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatographic (GPC) analyses on a Tosoh model SC-8010 instrument equipped with RI (Tosoh RI-8012) and MALLS (multiangle laser light scattering, Wyatt DAWN DSP instrument, $\lambda_0 = 632.8$ nm) detectors connected to the TSK gel

columns G1000, G2500, G4000, and G7000 in THF at 40 °C. The refractive index increment (d*n*/d*c*) of 0.128 mL/g, which had been reported for 1,4-*cis*-poly(1,3-butadiene) in THF,[19] was used for the calculations of the molecular weights of all the homopoly(1,3-butadiene)s, homopoly(isoprene)s, and poly(1,3-butadiene-*co*-isoprene)s in this study. EIMS measurements were performed on a JEOL JMS-SX102A mass spectrometer. Tensile tests were conducted on a Orientec RTC-1210 A universal testing instrument and measured at 25 °C with a crosshead speed of 50 mm/min.

Materials. Toluene and THF were dried over a sodium/potassium alloy and were distilled before use. Anhydrous $FeCl_2$, $FeCl_3$, 2,2′:6′,2″-terpyridine, 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine, 6,6″-dibromo-2,2′;6,′2″-terpyridine, 2-aminomethylpyridine, and (−)-sparteine were purchased from Aldrich. *N*-(2-Pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine was prepared according to the literature.[20]

Preparation of [Fe(2,2′:6′,2″-terpyridine)$_2$][FeCl$_4$]$_2$ (1). Terpyridine (1.0 g, 4.3 mmol) was added to a mixture of anhydrous $FeCl_2$ (0.5 g, 4.0 mmol) dissolved in 100 mL of THF in a two-necked round-bottomed flask equipped with a condenser and dropping funnel. The mixture was stirred magnetically for 10 h at 25 °C, resulting in the formation of a purple suspension. Resulting purple precipitates were collected by centrifugation and washed with a 1:2 mixture of THF and hexane (10 mL) followed by drying in vacuo. Thus, [Fe(terpyridine)$_2$][$FeCl_4$]$_2$ was obtained as a purple powder in 97.3%; mp > 260 °C. Anal. Calcd for $C_{30}H_{22}N_6Fe_3Cl_8$: C, 39.26; H, 2.42; N, 9.16. Found: C, 39.20; H, 2.41; N, 9.08.

Preparation of FeCl$_2$[6,6″-bis(3,5-dimethylphenyl)-2,2′:6′,2″-terpyridine] (2). The ligand 6,6″-bis(3,5-dimethylphenyl)-2,2′:6′,2″-terpyridine was prepared as follows. A solution of Pd(PPh$_3$)$_4$ (0.08 g, 0.07 mmol), 3,5-dimethylphenylboronic acid (1.15 g, 7.65 mmol), 6,6″-dibromo-2,2′:6′,2″-terpyridine (1.0 g, 2.56 mmol), and Na_3PO_4·12H_2O (4.09 g, 10.75 mmol) in a mixture of 1,2-dimethoxyethane (DME: 24 mL) and H_2O (4 mL) was refluxed for 20 h. The solution was evaporated to dryness, and the residue was extracted with benzene (80 mL). After washing with brine, the solution was dried over $MgSO_4$. The solution was concentrated to remain a white precipitate, which was collected with filtration, washed with diethyl ether, and dried in vacuo to yield the desired ligand in 83.7% yield. An analytically pure sample was obtained by recrystallization from a mixture of toluene and hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, 2H, 3′,5′-terpy), 8.61 (d, 2H, 3,3″-terpy), 8.05 (t, 1H, 4′-terpy), 7.92 (t, 2H, 4,4″-terpy), 7.81 (s, 4H, *o*-C$_6$*H*$_3$Me$_2$), 7.78 (d, 2H, 5,5″-terpy), 7.12 (s, 2H, *p*-C$_6$*H*$_3$Me$_2$), 2.47 (s, 12H, *m*-C$_6$H$_3$*Me*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8 (6,6″-terpy), 155.8 (2,2″-terpy), 155.5 (2′,6′-terpy), 139.4 (*ipso* or *m*-*C*$_6$H$_3$Me$_2$), 138.2 (*ipso* or *m*-*C*$_6$H$_3$Me$_2$), 137.7 (4′-terpy), 137.5 (4,4″-terpy), 130.7 (*p*-*C*$_6$H$_3$Me$_2$), 124.9 (*o*-*C*$_6$H$_3$Me$_2$), 121.3 (3′,5′-terpy), 120.4 (5,5″-terpy), 119.3 (3,3″-terpy), 21.5 (*m*-C$_6$H$_3$*Me*$_2$). Anal. Calcd for $C_{31}H_{27}N_3$: C, 84.32; H, 6.16; N, 9.52. Found: C, 84.37; H, 6.15; N, 9.37. EIMS for $C_{31}H_{27}N_3$ (relative ratio): *m*/*z* 441 (M^+, 100), 426 ($M^+ - CH_3$, 46). A mixture of $FeCl_2$ (0.16 g, 1.26 mmol), bis(3,5-dimethylphenyl)terpyridine (0.56 g, 1.26 mmol), and 30 mL of THF was refluxed for 24 h, generating a purple suspension. The precipitates were collected by centrifugation and washed with a mixture of THF and hexane (1:1 volume ratio, 30 mL) followed by drying in vacuo to give $FeCl_2$[bis(3,5-dimethylphenyl)terpyridine] in 79.8% yield; mp > 260 °C. Anal. Calcd for $C_{31}H_{27}N_3FeCl_2$: C, 65.52; H, 4.79; N, 7.39. Found: C, 65.05; H, 4.63; N, 7.40.

Preparation of FeCl$_2$[6,6″-bis(2,4,6-trimethylphenyl)2,2′:6′,2″-terpyridine] (3). The ligand 6,6″-bis(2,4,6-trimethylphenyl)-2,2′:6′,2″-terpyridine was prepared in the following manner. A solution of Pd(PPh$_3$)$_4$ (0.16 g, 0.14 mmol), 2,4,6-trimethylphenylboronic acid (2.4 g, 15.3 mmol), 6,6″-dibromo-2,2′:6′,2″-terpyridine (2.0 g, 5.1 mmol), and Na_3PO_4·12H_2O (8.2 g, 21.4 mmol) in a mixture of DME (48 mL) and H_2O (8 mL) was refluxed for 20 h. The solution was evaporated to dryness, and the residue was extracted with benzene (100 mL). After washing with brine, the solution was dried over $MgSO_4$. The solution was concentrated to remain a white precipitate, which was collected with filtration, washed with diethyl ether, and dried in vacuo to yield the desired compound in 77.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, 2H, 3,3″-terpy), 8.43 (d, 2H, 3′,5′-terpy), 7.92 (t, 2H, 4,4″-terpy), 7.80 (t, 1H, 4′-terpy), 7.33 (d, 2H, 5,5″-terpy), 6.96 (s, 4H, *m*-C$_6$*H*$_2$Me$_3$), 2,-32 (s, 6H, *p*-C$_6$H$_2$*Me*$_3$), 2.05 (s, 12H, *o*-C$_6$H$_2$*Me*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (2,2″-terpy), 156.1 (3′,5′-terpy), 155.6 (6,6″-terpy), 138.0 (*ipso* or *o* or *p*-*C*$_6$H$_2$Me$_3$), 137.6 (4′-terpy), 137.5 (*ipso* or *o* or *p*-*C*$_6$H$_2$Me$_3$), 136.9 (4,4″-terpy), 135.9 (*ipso* or *o* or *p*-*C*$_6$H$_2$Me$_3$), 128.4 (*m*-*C*$_6$H$_2$Me$_3$), 124.8 (5,5″-terpy), 121.4 (3′,5′-terpy), 118.8 (3,3″-terpy), 21.1 (*p*-C$_6$H$_2$*Me*$_3$), 20.4 (*o*-C$_6$H$_2$*Me*$_3$). Anal. Calcd for $C_{33}H_{31}N_3$: C, 84.40; H, 6.65; N, 8.95. Found: C, 83.83; H, 6.82; N, 8.58. EIMS for $C_{33}H_{31}N_3$ (relative ratio): *m*/*z* 469 (M^+, 100), 454 ($M^+ - CH_3$, 3).

A mixture of $FeCl_2$ (0.013 g, 0.11 mmol), 6,6″-bis(2,4,6-Me$_3$-C$_6$H$_2$)terpyridine (0.05 g, 0.12 mmol), and 10 mL of THF was refluxed for 24 h, resulting in the formation of a purple suspension. The precipitates were collected by centrifugation and washed with a mixture of THF and hexane followed by drying in vacuo to give $FeCl_2$[6,6″-(2,4,6-Me$_3$C$_6$H$_2$)terpyridine in 90.1% yield; mp > 260 °C. Anal. Calcd for $C_{33}H_{31}N_3FeCl_2$: C, 65.46; H, 5.23; N, 7.04. Found: C, 65.40; H, 5.18; N, 6.99. EIMS for $C_{33}H_{31}N_3{}^{56}Fe^{35}Cl_2$(relative ratio): *m*/*z* 596 (M^+, 4), 470 ($M^+ - FeCl_2 + H$, 100).

Preparation of FeCl$_3$(2,2′:6′,2″-terpyridine) (4). 2,2′:6′,2″-Terpyridine (1.5 g, 6.2 mmol) was added to $FeCl_3$ (1.0 g, 6.2 mmol) dispersed in 100 mL of THF, and the mixture was stirred for 10 h at 25 °C, resulting in the formation of yellow suspension. From the suspension, the desired yellow powder of $FeCl_3$(terpyridine) was obtained by centrifugation in 93. 5% yield; mp > 260 °C. Anal. Calcd for $C_{15}H_{11}N_3FeCl_3$: C, 45.56; H, 2.80; N, 10.63. Found: C, 45.60; H, 2.82; N, 10.68. EIMAS for $C_{15}H_{11}N_3{}^{56}Fe^{35}Cl_3$ (relative ratio): *m*/*z* 395 (M^+, 6), 233 ($M^+ - FeCl_3$, 100).

Preparation of FeCl$_3$(4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine) (5). 4,4′,4″-Tri-*tert*-butyl-2,2′:6′,2″-terpyridine (1.0 g, 2.5 mmol) was added to $FeCl_3$ (0.4 g, 2.5 mmol) dispersed in 100 mL of THF, and the mixture was stirred for 10 h at 25 °C, resulting in the formation of yellow suspension. From the suspension, the desired yellow powder of $FeCl_3$(*t*Bu$_3$-terpyridine) was obtained by centrifugation in 93. 5% yield; mp > 260 °C. Anal. Calcd for $C_{27}H_{34}N_3FeCl_3$: C, 57.62; H, 6.09; N, 7.47. Found: C, 57.47; H, 6.08; N, 7.25. EIMAS for $C_{27}H_{35}N_3{}^{56}Fe^{35}Cl_3$ (relative ratio): *m*/*z* 562 (M^+, 4), 401 ($M^+ - FeCl_3$, 100).

Preparation of FeCl$_2$[*N*-(2-pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine] (6). A mixture of $FeCl_2$ (0.11 g, 0.87 mmol), *N*-(2-pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine[20] (0.28 g, 0. 87 mmol), and 45 mL of THF was placed in a 300 mL two-necked round-bottomed flask. The reaction mixture was stirred for 24 h at ambient temperature, resulting in the formation of purple solution. After centrifugation, the solution was evaporated to dryness. The residue was washed with hexane (20 mL) to give $FeCl_2$[*N*-(2-pyridyl)-methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine] as a black powder in 90% yield; mp > 260 °C. Anal. Calcd for $C_{21}H_{28}ON_2FeCl_2$: C, 55.78; H, 6.46; N, 6.19. Found: C, 55.24; H, 6.48; N, 6.20.

Preparation of FeCl[*N*-(2-pyridyl)methyl-2-oxy-3,5-di-*tert*-butylbenzaldimine] (7). To a solution of *N*-(2-pyridyl-9-methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine (1.48 g, 4.5 mmol) in THF (45 mL) held at 0 °C was added dropwise butyllithium in hexane (1.50 M, 3.1 mL, 4.9 mmol). The solution was stirred for 3 h at 25 °C and then added to a stirred solution of $FeCl_2$ (0.58 g, 4.5 mmol) in THF (30 mL). After stirring the mixture for 10 h, the solution was evaporated to dryness. The residue was washed with hexane (20 mL) to generate FeCl[*N*-(2-pyridyl)methyl-2-oxy-3,5-di-*tert*-butylbenzaldimine] as a black powder in 45.6% yield (0.85 g, 2.05 mmol). Anal. Calcd for $C_{21}H_{27}ON_2FeCl$: C, 60.81; H, 6.56; N, 6.75. Found: C, 61.11; H, 6.76; N, 6.51. EIMS for $C_{14}H_{20}N_2{}^{56}Fe^{35}Cl_2$: *m*/*z* 414 ($M^+$, 3), 323 ($M^+ - FeCl_2$, 100).

Preparation of FeCl$_2$(sparteine) (8). A mixture of anhydrous $FeCl_2$ (1.48 g, 11 mmol), (−)-sparteine (2.59 g, 11 mmol), and 100 mL of THF was placed in a 300 mL two-necked round flask. The mixture was stirred for 10 h at 25 °C. After

centrifugation of the mixture, the supernatant liquid was concentrated and cooled to −25 °C to induce the pale-yellow crystals of $FeCl_2$(sparteine) in 34.2% yield; mp 216−218 °C. Anal. Calcd for $C_{15}H_{26}N_2FeCl_2$: C, 49.89; H, 7.26; N, 7.76. Found: C, 49.81; H, 7.23; N, 7.61. EIMS for $C_{15}H_{26}N_2{}^{56}Fe^{35}Cl_2$: *m*/*z* 360 ($M^+$, 3), 234 (sparteine, 100).

Homopolymerizations of 1,3-Butadiene and Isoprene. To a 20 mL Schlenk tube kept at −78 °C was introduced 1,3-butadiene (1.74 mL, 20 mmol) and toluene (5 mL) (1,3-butadiene was once transferred into a rubber balloon from the cylinder and then trapped in a cold tube). An initiator (0.1 mmol) and modified methylalumoxane (MMAO) (10 mmol) were added to this solution at −78 °C. Then the Schlenk tube was sealed off using a gas burner. The mixture was hold at 30 °C for 12 h and poured into excess methanol to induce the precipitation of polymer. The resulting methanol-insoluble polymer was dried in vacuo. In essentially the same way, isoprene (2.0 mL, 20 mmol) was polymerized using an initiator (0.1 mmol) with MMAO (10 mmol) for 12 h at 25 °C, and the resulting polymer was dried in vacuo.

Random Copolymerization of 1,3-Butadiene with Isoprene. 1,3-Butadiene (1.74 mL, 20 mmol) was introduced into a 20 mL Schlenk tube cooled to −78 °C by trap-to-trap distillation and isoprene (2.0 mL, 20 mmol) dissolved in 10 mL of toluene was added, and an initiator (0.1 mmol)/MMAO (10 mmol) was added to the mixture. After sealing off the tube by a gas burner, the mixture was stirred for 12 h at 25 °C, and then the content of tube was poured into excess methanol to precipitate the polymer. The resulting polymer was dried in vacuo.

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Supporting Information Available: Molecular structures of **1**, **2**, **4**, and **8** including their ORTEP drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

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