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Facile Syntheses of Bis[1-(arylimino)ethyl]pyridine−$MoCl_3$/MMAO Catalytic Systems and Their Dual Catalytic Functions for ROMP of Norbornene and Linear Polymerization of Ethylene

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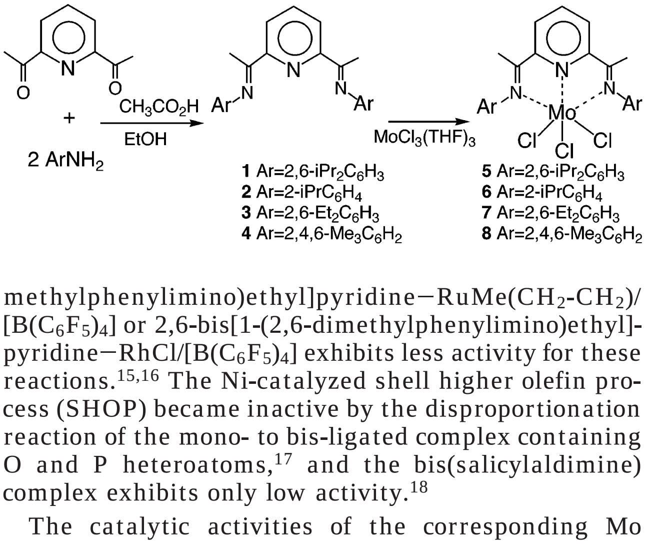
ABSTRACT: ROMP (ring-opening metathesis polymerization) of norbornene using a series of 2,6-bis[1-(arylimino)ethyl]pyridine−$MoCl_3$/cocatalyst systems was explored, and the 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine−$MoCl_3$ (**5**)/MMAO (modified methylaluminoxane, AlMeO:Al-isoBuO = 3:1) system particularly exhibits a high catalytic activity at 60 °C for norbornene polymerization leading to high molecular weight polymers with high cis contents (98−100%). The 2,6-bis[1-(arylimino)ethyl]pyridine−$MoCl_3$/$AlEt_3$ systems catalyzed the norbornene polymerization in high yields, but the cis selectivities were rather low. The **5**/MMAO system is also effective for the polymerization of *endo*-dicyclopentadiene at 60 °C, leading to soluble polymers with 100% cis content, and for the polymerization of ethylene with high activity (44.5×10^3 g of PE/(mol h)) to lead to linear polymers ($M_n = 16.8 \times 10^4$). Attempts to prepare ethylene−norbornene block copolymers failed, and a mixture of homopoly(norbornene) and homopoly(ethylene) was obtained.

Introduction

A variety of highly electrophilic and coordinately unsaturated alkylidyne or alkylidene complexes of molybdenum and tungsten containing bulky alkoxide ligands such as $W(CR)(O\text{-}2,6\text{-}C_6H_3\text{-}{}^iPr_2)_3$,[1] $Mo(CR)[OCMe(CF_3)_2]_3$,[2] $W(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}{}^iPr_2)[OCMe(CF_3)_2]_2$,[3] and $Mo(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}{}^iPr_2)(O\text{-}t\text{-}Bu)_2$[4] were found to exhibit the excellent ROMP activity for norbornene, 2,3-bis(trifluoromethyl)norbornadiene,[5] 2,3-bis(carbomethoxy)norbonadiene,[6] and 7,8-bis(trifluoromethyl)tricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene,[7] and the cyclic polymerization activity for α,ω-akanediynes,[8] to give the corresponding polymers which have novel uses and properties.[9] The cis selectivity for poly(norbornene) using $W(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}{}^iPr_2)[OCMe(CF_3)_2]_2$[3] is >95%, and the resulting polymers exhibit M_n of >40 000 and M_w/M_n of 1.02. The $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$-initiated polymerization of 2,3-bis(trifluoromethyl)norbornene produces >98% trans double bonds as determined by ^{13}C NMR. Thus, trans−cis selectivity changes depending on the electronic and steric effect of the alkoxide group bound to Mo or W together with the effect of substitution on the norbornene or norbonadiene molecules. Well-defined organometallic species, such as $Ta(CH\text{-}t\text{-}Bu)(S\text{-}2,4,6\text{-}C_6H_2\text{-}{}^iPr_3)_3(THF)$, have also showed high catalytic activity toward the ROMP of norbornene, i.e., M_n reaches 59 000 ($M_w/M_n = 1.05$), whereas the selectivity is very poor (trans, 55−67%).[10] These initiators have no catalytic activity for linear polymerizations of ethylene and 1-olefins. For these complexes, only the metathesis reaction occurs upon the addition of olefins.

Brookhart et al. reported the high catalytic activity of $Fe(II)Cl_2$ or $Co(II)Cl_2$ complexes in the presence of MMAO for the oligomerization[11] and preparation of high molecular weight polyethylene.[12−14] These complexes have a 2,6-bis[1-(2-*tert*-butylphenylimino)ethyl]pyridine ligand that tolerates heteroatoms. The reaction mode changes depending upon the steric bulkiness of the ligands. However, the corresponding 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine−$RuMe(CH_2\text{-}CH_2)$/$[B(C_6F_5)_4]$ or 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine−RhCl/$[B(C_6F_5)_4]$ exhibits less activity for these reactions.[15,16] The Ni-catalyzed shell higher olefin process (SHOP) became inactive by the disproportionation reaction of the mono- to bis-ligated complex containing O and P heteroatoms,[17] and the bis(salicylaldimine) complex exhibits only low activity.[18]

Scheme 1



The catalytic activities of the corresponding Mo complex for the polymerizations of ethylene and norbornene were previously unknown. In this paper we report high catalytic activities of 2,6-bis[1-(arylimino)ethyl]pyridine−$MoCl_3$/MMAO systems toward both the ROMP of norbornene and the linear polymerization of ethylene. ROMP of *endo*-dicyclopentadiene using the 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine−$MoCl_3$ (**5**)/MMAO system produced the desired polymer with 100% cis selectivity. Some attempts using the **5**/MMAO catalyst system for the block copolymerization of ethylene with norbornene are also reported.

Results and Discussion

Synthesis of 2,6-Bis[1-(arylimino)ethyl]pyridine−$MoCl_3$. A series of ligands were prepared easily by reacting 2,6-diisopropylaniline (**1**), 2-isopropylaniline (**2**), 2,6-diethylaniline (**3**), or 2,4,6-trimethylaniline (**4**) with 2,6-diacetylpyridine to give the corresponding 2,6-bis[1-(arylimino)ethyl]pyridine (Scheme 1). Elemental

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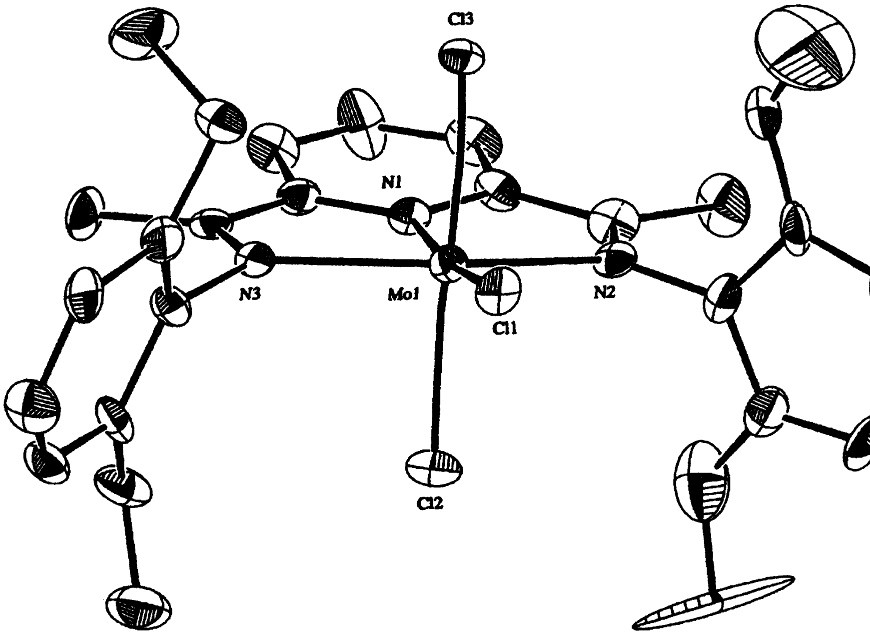
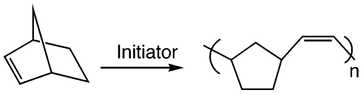


Figure 1. ORTEP drawing of complex **7**.

Scheme 2



analyses of the resulting products confirmed the formation of these ligands in high yield, whose structures were further characterized by ^1H NMR spectra (see Experimental Part). These ligands were reacted with a stoichiometric amount of $MoCl_3(THF)_3$ in THF to generate $MoCl_3$ complexes, 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine−$MoCl_3$ (**5**), 2,6-bis[1-(2-isopropylphenylimino)ethyl]pyridine−$MoCl_3$ (**6**), 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine−$MoCl_3$ (**7**), and 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine−$MoCl_3$ (**8**), in reasonable yields. As a typical example, the X-ray structure determination of 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine−$MoCl_3$ (**7**) was carried out. The complex assumes the distorted octahedral geometry and exhibits C_{2v} symmetry about the Cl(1)−Mo−N(1) plane. The molecular structure of **7** is illustrated in Figure 1. Each aryl plane crosses at a right angle with another aryl plane, and the plane of aryl groups also crosses at a right angle with the Mo−N(1)−N(2)−N(3) plane. The Mo−N(pyridine) bond distance [2.06(2) Å] is a little longer than the Mo−N(imino) bond [2.18(2) and 2.22(2) Å], in good agreement with the corresponding Fe complex [Fe−N(pyridine) 2.088(4) Å, Fe−N(imino) 2.238(4) and 2.250(4) Å].[10] The three Mo−Cl distances are nearly identical.

ROMP of Norbornene with Complexes 5−8/Cocatalyst Systems. ROMP of norbornene was carried out using complexes **5**−**8** combind with an equivalent of $AlEt_3$. The polymerization was performed in toluene at various temperatures for 6 h. These initiators were ineffective for the polymerization of norbornene at temperatures below −40 °C, but above 25 °C, the yields and molecular weights increase with increasing temperature. Especially complexes **5**−**7** produce the polymers quantitatively at 60 °C (Table 1). The cis content of the polymers is >90% using complexes **6** and **7** at 0 °C. When the polymerization period was shortened to 5 min at 0 °C, characteristic features were observed for each system. For example, complex **5** gives rise to high yields of poly(norbornene), 99% ($M_n = 14.0 \times 10^4$, $M_w/M_n = 1.40$, cis content 77%), while **6**, **7**, and **8** showed rather low yields, 30, 7, and 18%, respectively, to give polymers with $M_n = (22-44) \times 10^4$, $M_w/M_n = 1.4-1.8$, and cis content 74−88%, presumably due to the poor steric bulkiness of ligands. Thus, the bulkiness of substituents at 2 and 6 positions plays an important role in controlling the polymer yields.

Table 1. ROMP of Norbornene with Molybdenum Complexes 5−8/$AlEt_3$[a]

complex	temp (°C)	yield (%)	$M_n^b \times 10^{-4}$	M_w/M_n^b	cis content[c] (%)
5	0	99	23.7	1.37	78
	25	100	25.0	1.40	70
	60	100	25.9	1.54	68
6	0	99	27.0	1.37	90
	25	100	28.3	1.47	84
	60	100	30.2	1.50	73
7	0	38	7.5	1.38	91
	25	100	24.1	1.33	85
	60	100	53.6	1.50	79
8	0	2	15.3	1.47	87
	25	16	18.1	1.49	86
	60	93	29.5	1.68	77

[a] Conditions: 0.5 mL of toluene for 6 h, $[\text{monomer}]_0 = 2$ mmol, $[\text{Mo}]_0 = 0.02$ mmol, $[AlEt_3]_0 = 0.02$ mmol. [b] Determined by GPC. [c] Determined by ^1H NMR.

By using MMAO as a cocatalyst in place of $AlEt_3$, we could realize high cis selectivity (99−100%) for the polymerization of norbornene in high yields, 99−100%, when we used **5**/MMAO system for 12 h (Table 2). Catalyses of **6**−**8**/MMAO systems are also very high even when the polymerizations were carried out for a short period, 1 h. However, the **5**/MMAO system gives rise to the formation of polymers with very narrow molecular weight distribution, $M_w/M_n = 1.38$, as compared with those obtained by **6**−**8**/MMAO systems, due to the ideal steric bulkiness of the 2,6-diisopropylphenylimino group.

The reaction should be initiated by the Mo−carbene species, $-Mo{=}CHCH_3$ or $-Mo{=}CH_2$, formed from complexes **5**−**8** and $AlEt_3$ or MMAO. Since the Mo complex/

Table 2. ROMP of Norbornene with Molybdenum Complexes 5−8/MMAO[a]

complex	cocatalyst	time (h)	temp (°C)	yield (%)	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	cis content[c] (%)
5	MAO	12	60	99	48.6	1.56	63
	MMAO	12	0	99	9.5	1.36	100
	MMAO	12	25	99	15.9	1.39	99
	MMAO	12	60	100	54.8	1.45	98
	MMAO	1	60	71	41.7	1.38	98
6	MMAO	1	60	82	59.2	1.92	98
7	MMAO	1	60	77	82.3	2.05	95
8	MMAO	1	60	89	90.2	2.61	97

[a] Conditions: 0.5 mL of toluene, $[\text{monomer}]_0 = 2$ mmol, $[\text{Mo}]_0 = 0.02$ mmol, $[\text{MMAO}]_0 = 6.0$ mmol. [b] Determined by GPC. [c] Determined by ^{1}H NMR.

Table 3. ROMP of Norbornene with Molybdenum Complexes 5/Cocatalyst System[a]

cocatalyst	$[\text{cocat.}]_0/[\text{Mo}]_0$ (mol/mol)	temp (°C)	time (min)	yield (%)	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	cis content[c] (%)
$AlMe_3$	1	60	60	70	39.9	1.44	62
	3	60	60	45	40.3	1.58	62
Et_2AlCl	1	60	60	89	38.1	1.39	58
	3	60	60	56	39.0	1.48	55
BzMgCl	1	60	10	99	13.8	2.91	63
	2	60	10	100	21.3	2.35	62
	3	60	10	100	32.7	2.23	62
	5	60	10	32	9.2	3.49	42
BzMgCl	1	25	10	50	9.8	2.64	69
	2	25	10	84	14.1	3.50	69
	3	25	10	83	9.2	4.80	67
	5	25	10	5	35.3	1.37	57
Me_3SiCH_2MgCl	1	60	10	99	16.0	2.28	71
	2	60	10	99	11.5	3.23	66

[a] Conditions: 0.5 mL of toluene, $[\text{monomer}]_0 = 2$ mmol, $[\text{Mo}]_0 = 0.02$ mmol. [b] Determined by GPC. [c] Determined by ^{1}H NMR.

MMAO system produced highly cis selective polymers, the resulting $(L)ClMo{=}CHR$ species should interact with the MMAO molecule, allowing control of the selectivity. It is very difficult to obtain the exact evidence by NMR for formation of $Mo{=}CHR$ species since the resulting Mo species is paramagnetic even in the presence of MMAO.

To gain further insights into the reaction mechanism, we used $C_6H_5CH_2MgCl$ or Me_3SiCH_2MgCl in place of $AlMe_3$ and $AlEt_2Cl$ as a cocatalyst, since these compounds are known to be effective in producing Mo−carbene species. The yield increased by the addition of 2 equiv of such magnesium compound for 10 min, indicating the formation of Mo−carbene species at 60 °C. The reaction at a lower temperature, 25 °C, is ineffective for formation of such a carbene species (Table 3). The addition of $AlMe_3$ or $AlEt_2Cl$ in the molar ratio of $[\text{Al}]_0/[\text{Mo}]_0 = 1-3$ showed reduced yields even when the reaction was carried out for longer period, 60 min, although the resulting molecular weight distributions are very low.

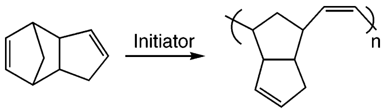
Poly(norbornene) obtained by ROMP method exhibits double bonds in the main chain, and therefore these materials are readily oxidized during the molding process to result in the formation of insoluble polymer. Therefore, hydrogenation of the resulting poly(norbornene) was carried out to improve the chemical properties. As a consequence, T_m of the polymer obtained from *cis*-95% poly(norbornene) was 142 °C, while that from *cis*-20% poly(norbornene) was only 102 °C because of the presence of small syndiotactic bias.[19]

Table 4. ROMP of *endo*-Dicyclopentadiene with Molybdenum Complexes 5/Cocatalyst System[a]

cocatalyst	temp (°C)	yield (%)	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	cis content[c] (%)	T_g (°C)
MMAO	25	16	9.4	2.05	92	159
	60	39	25.6	1.45	100	160
$AlEt_3$	25	43	47.5	1.28	35	156
	60	86	85.0	1.15	51	156

[a] Conditions: 0.5 mL of toluene for 3 h, $[\text{monomer}]_0 = 2$ mmol, $[\text{Mo}]_0 = 0.02$ mmol, $[\text{AlEt}_3]_0/[\text{Mo}]_0 = 1.0$ mol/mol,$[\text{MMAO}]_0/[\text{Mo}]_0 = 1\ 00$ mol/mol. [b] Determined by GPC. [c] Determined by ^{1}H NMR.

Scheme 3



Dicyclopentadiene Polymerizations with Complex 5/Cocatalyst Systems. ROMP of dicyclopentadiene is expected to produce very ligid main chain due to the presence of a [3.0.3]-bicyclooctane ring. Although the polymerization of dicyclopentadiene was reported using $TiCl_4(L)_2/MeLi$,[20] $WOCl_4/Me_4Si$,[21] and Ru−carbene·PPh_3 systems,[22] stereospecific polymerization was not yet realized and cross-linking occurred very fluently in many cases. However, Schrock's catalyst[23] and Grubbs's catalyst[22] systems produce completely soluble poly(dicyclopentadiene) without the cross-linking. Since the complex **5**/MMAO system can perform the highly cis-selective ROMP for norbornene, we have attempted the polymerization of *endo*-dicyclopentadiene here (Table 4). As a result, the **5**/MMAO system produces soluble poly(dicyclopentadiene) with high cis selectivity (100%) in 39% yield when the polymerization was carried out at 60 °C. (Only <5% of the resulting polymer is insoluble in $CHCl_3$ by cross-linking.) The T_g values (156−160 °C) are higher irrespective of the cis content than those obtained for conventional polymers starting from endo−exo mixture which exhibit T_g of ca. 110 °C. When $AlEt_3$ was used as a cocatalyst, the polymer yield increased to 85%, but the cis content decreased to 51%. The M_w/M_n value becomes very small in this case.When *cis*-20% poly(dicyclopentadiene) was hydrogenated with $(Cy_3P)_2$-

Table 5. Ethylene Polymerizations with Complexes 5−8/MMAO Systems[a]

complex	temp (°C)	time (min)	activity, 10^3 g of PE/(mol h)	M_n[b] × 10^4	M_w/M_n[b]	T_g[c] (°C)
5	25	60	49.8	21.02	3.4	140
6	25	60	3.4	0.28	123.7	135
7	25	60	0.9	0.07	5.1	
8	25	60	1.1	0.11	23.3	
5	−78	20	1.2	0.98	4.3	
5	0	20	41.1	25.98	3.6	139
5	25	20	44.5	16.82	2.3	138
5	60	20	2.1	1.12	33.4	

[a] Conditions: 0.5 mL of toluene, $[Mo]_0 = 0.01$ mmol, $[MMAO]_0/[Mo]_0 = 500$ mol/mol. [b] Determined by GPC. [c] Determined by DSC.

RuCl═CHPh catalyst in hexane at 160 °C, its T_g value (105 °C) is identical with those from atactic poly(dicyclopentadiene) (100 °C). However, the hydrogenation of 92% *cis*-poly(dicyclopentadiene) produced a polymer with higher T_g and was as high as 145 °C, presumably due to the high syndiotacticity.[17] Thus, a high T_g value of hydrogenated poly(dicyclopentadiene) was realized for the first time using the **5**/MMAO system followed by hydrogenation using a Ru catalyst. Hydrogenation with $PdCl_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ is also effective.

Ethylene Polymerizations with Complexes 5−8/Cocatalyst Systems. Mo−carbene complexes are usually ineffective for the polymerization of ethylene and olefins, since such complexes exhibit high activity only for the metathesis reaction. However, Brookhart[10−13] found that bis(iminopyridine) complexes of Fe and Co exhibited good catalytic activity for the polymerization of ethylene. Therefore, we have examined the catalytic activities of the above-noted Mo complexes **5**−**8** toward the polymerizations of ethylene. Complexes **5**−**8** themselves are completely inert for polymerization of ethylene. However, when the polymerization was carried out at ambient temperature for 60 min in the presence of MMAO, the **5**/MMAO system exhibits high catalytic activity, leading to high molecular weight polymers ($M_n = 21.02 \times 10^4$) with relatively low polydispersity, $M_w/M_n = 3.4$ (Table 5). The resulting polymer exhibits a completely linear structure as evidenced by ^{13}C NMR (singlet peak at 29.8 ppm in 1,2,4-trichlorobenzene). To optimize the reaction conditions, the effect of polymerization temperatures was studied between −78 and 60 °C. As a result, the optimal operating temperatures were found to be between 0 and 25 °C. The complexes are susceptible to deactivation above 60 °C under polymerization conditions. $AlEt_3$, $AlEt_2Cl$, and MAO (methylaluminoxane) are ineffective as cocatalyst compared with MMAO (Table 6). Careful experiments showed that the activity and molecular weight increase proportionally to the molar MMAO/**5** ratio up to a ratio of 500, and further addition of MMAO (MMAO/**5** = 1000) significantly reduced the catalytic activity. Molecular weight distribution reveals the lowest value when we used $[MMAO]_0/[Mo]_0$ molar ratio of 500. The use of $AlEt_3$ and $AlEt_2Cl$ is ineffective for polymerization of ethylene.

Attempts To Perform the Copolymerizations of Ethylne with Norbornene. Random or block copolymerizations of ethylene with norbornene derivatives should produce characteristic polymer materials reflecting the presence of a hard poly(norbornene) segment. Vinylic copolymerizations of these two monomers have already been reported by several workers.[15,26−28] Crystallinity of the copolymer decreased significantly by introduction of a trace amount of norbornene in the polyethylene chain. The copolymerization of styrene with norbornene was also reported using Ni-based/MMAO catyalysts.[29] These polymers are useful as prominent optical materials since these exhibit high transparency, high refractive index, low density, and high stiffness. Since the vinylic polymerization of a cyclic olefin is known to switch the mechanism of polymerization mode from vinylic to ROMP type polymerization by the addition of a stoichiometric amount of phenylacetylene after completion of the vinyl polymerization,[25,26] we explored the ethylene polymerization followed by the addition of phenylacetylene and norbornene. As a result, such a change in mechanism was not observed in this case. The resulting chloroform soluble fraction was composed of only poly(norbornene) as evidenced by ^{1}H NMR, and the chloroform-insoluble fraction was poly(ethylene) as identified by ^{13}C NMR. Of course, polymerization of ethylene followed by the addition of norbornene in the absence of phenylacetylene or the polymerization of norbornene followed by the addition of ethylene does not generate the expected block copolymers. The GPC profile shows a bimodal pattern, and the resulting poly(norbornene)/poly(ethylene) ratio for the former case is 55/45 [M_n of poly(ethylene), 15.8×10^4] and for the latter case is 67/33 [M_n of poly(ethylene), 16.8×10^4] (Table 7).

Thus, we failed in synthesizing a block copolymer between ethylene and norbornene using the **5**/MMAO system.

The **5**/MMAO system showed high catalytic activity (yields > 99%) for the polymerization of norbonadiene, but the polymers were all insoluble in common solvents, presumably due to the cross-linking. This system is inert to the polymerizations of cyclopentene, *endo*-5,6-dicarbomethoxybicyclo[2.2.1]hept-2-ene, methyl methacrylate, isoprene, and styrene.

Table 6. Ethylene Polymerizations with Complexes 5/Cocatalyst Systems[a]

cocatalyst	Al/Mo (mol/mol)	time (min)	activity, 10^3 g of PE/(mol h)	M_n[b] × 10^4	M_w/M_n[b]	T_g[c] (°C)
MAO	300	180	6.9	0.34	125.4	134
MMAO	100	20	0.8	2.02	60.35	135
	200	20	7.9	2.58	25.4	136
	300	20	34.0	5.80	7.9	138
	500	20	44.5	16.82	2.3	138
	1000	20	20.5	11.46	3.4	137
$AlEt_3$	10	300	*d*			
	100	300	*d*			
$AlEt_2Cl$	100	300	0.0			

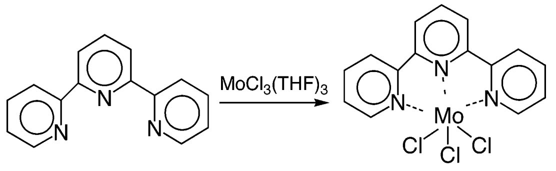
[a] Conditions: 0.5 mL of toluene, $[Mo]_0 = 0.01$ mmol, Polymerization temperature 25°C. [b] Determined by GPC. [c] Determined by DSC. [d] Trace.

Table 7. Poly(norbornene) Fraction Obtained by Copolymerization of Ethylene with Norbornene Using 5/MMAO[a]

Al/Mo	yield of poly(norbornene)	activity, 10^3 g of PE/(mol h)	$M_n{}^d \times 10^4$	$M_w/M_n{}^d$	cis content[e] (%)
500[a]	58	4.4×10^4	8.1	1.64	94
500[b]	72	2.4×10^4	20.8	1.27	100
500[c]	70	1.0×10^4	42.3	2.02	100

[a] Conditions: 0.5 mL of toluene, $[\mathrm{Mo}]_0 = 0.02$ mmol, $[\text{norbornene}]_0/[\mathrm{Mo}]_0 = 300$ mol/mol, temperature 25 °C. [b] Norbornene polymerization for 12 h and then ethylene polymerization for 1 h. [c] Ethylene polymerization for 20 min and then norbornene polymerization for 12 h. [d] Ethylene polymerization for 20 min, addition of phenylacetylene (phenylacetylene/Mo = 2 mol/mol), and then norbornene polymerization for 12 h. [e] Determined by GPC. [f] Determined by ^{1}H NMR.

Scheme 4



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ROMP of Norbornene with Complex 9/BzMgBr System. In an attempt to further enhance the activity of the catalyst, we have also explored the catalytic action of 2,2′:6′,2″-terpyridine-MoCl$_3$ (**9**), since the complex **5** having three nitrogen groups in a molecule exhibits good catalytic activity for polymerization of norbornene. We can prepare the desired complex in excellent yields (93%) at relatively low cost. However, the catalytic activity was not as high (even in the presence of MMAO or benzylMgBr) as the **5**/MMAO system. The polymer yield was <16% at 60 °C in toluene, and M_n was only $<3.6 \times 10^3$. Furthermore, the cis selectivity was 60%. Thus, the terpyridine complex lacks the high catalytic activity, presumably due to the absence of substituents at the 6- and 6″-positions, which decreased the complex's steric bulkiness.

Conclusion

The 2,6-bis[1-(arylimino)ethyl]pyridine−MoCl$_3$/MMAO systems showed high catalytic activities toward both the ROMP of norbornene or *endo*-dicyclopentadiene and the linear polymerization of ethylene. Complexes with dual catalytic activities for both ROMP and olefin polymerization have not been reported until now. The attempts for the block copolymerization of ethylene with norbornene failed, and a mixture of homopoly(norbornene) and homopoly(ethylene) was obtained by the addition of these two monomers.

Experimental Part

General Data. All operations were conducted with standard Schlenk techniques under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL model JNM-400 (400 MHz for ^{1}H nucleus and 100 MHz for ^{13}C nucleus) or a JEOL model EX 270 instruments. ^{1}H NMR chemical shifts were calibrated using chloroform (δ 7.26 ppm) in chloroform-*d* or benzene (δ 7.20 ppm) in benzene-d_6. The number- and weight-average molecular weights of poly(norbornene) were determined by gel permeation chromatography (GPC) on a Tosoh model SC 8010 chromatograph equipped with columns TSK gel G1000$_{\mathrm{HR}}$, G2500$_{\mathrm{HR}}$, G4000$_{\mathrm{HR}}$, and G7000$_{\mathrm{HR}}$ using chloroform as an eluent at 40 °C. The flow rate was 1.0 mL min^{-1}. The molecular weights were determined by using universal curve plotted with standard polystyrene, whose M_w values were measured by a light-scattering method. Molecular weights of poly(ethylene) were determined by GPC on a Waters 150C model equipped with Shodex 806M column, using 1,2,4-trichlorobenzene as an eluent at 140 °C. EIMS (electron impact mass spectrum) was recorded on a JEOL JMS-SX 102A mass spectrometer at 30 eV. Elemental analysis was performed on a Perkin-Elmer-2400 series II CHNS/O analyzer. The glass transition temperatures (T_g) of polymers were obtained using a Seiko SSC5100-DSC22C apparatus.

Materials. Solvents such as tetrahydrofuran, hexane, and toluene were distilled from Na/K-benzophenone under an argon atmosphere before use. Norbornene was purchased from Aldrich, dried on CaH$_2$ for 1 week in THF, and distilled before use. Dicyclopentadiene containing an endo/exo isomer in a 99.3/0.6 molar ratio was a gift from Nippon Zeon. Co. and was distilled before use. Ethylene was purchased from Koatsu Gas Kogyo Co. and dried over phosphorus pentoxide. MMAO and MAO were given by Tosoh Fine Chem. Co. and used without further purification. 2,6-Diisopropylaniline, 2-isopropylaniline, 2,6-diethylaniline, and 2,4,6-trimethylaniline were purchased from Tokyo Kasei Kogyo Co. and used after distillation. MoCl$_5$(THF)$_3$, benzylMgBr (2.0 M solution of THF), and 2,6-diacetylpyridine were purchased from Aldrich and used without further purification.

Synthesis of 2,6-Bis[1-(2,6-diispropylphenylimino)ethyl]pyridine (1). To a solution of 2,6-diacetylpyridine (1.50 g, 9.2 mmol) in absolute ethanol (25 mL) was added 2,6-diisopropylaniline (3.64 mL, 18.4 mmol). Afer the addition of a few drops of glacial acetic acid, the solution was refluxed overnight. Upon cooling the solution to room temperature, the product was crystallized from ethanol to give 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine as yellow crystals (3.54 g) in 80% yield. ^{1}H NMR (CDCl$_3$): δ 8.57 (d, 2H, py−Hm), 7.95 (t, 1H, py−Hp), 7.1 (m, 6H, Ar−H), 2.79 (sept, 4H, CHMe$_2$), 2.27 (s, 6H, N═CMe), 1.17 (d, 24H, CHMe$_2$). Anal. Calcd for C$_{33}$H$_{43}$N$_3$: C, 82.28; H, 9.00; N, 8.72. Found: C, 82.29, H, 8.86; N, 8.55.

Syntheses of Other 2,6-Bis[1-(alkylphenylimino)ethyl]pyridine (2−4). In place of 2,6-diisopropylaniline, 2-isopropylaniline, 2,6-diethylaniline, or 2,4,6-trimethylaniline was added to 2,6-diacetylpyridine in absolute ethanol to give 2,6-bis[1(2-isopropylphenylimino)ethyl]pyridine (**2**), 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine (**3**), or 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine (**4**), respectively, as yellow crystals in 41%, 22%, and 32% yields. **2**: ^{1}H NMR (CDCl$_3$): δ 8.37 (d, 2H, Py-Hm), 7.88 (t, 1H, Py−Hp), 7.30 (d, 2H, Ar−H3), 7.17 (t, 2H, Ar−H5), 7.10 (t, 2H, Ar−H4), 6.93 (d, 2H, Ar−H5), 2.99 (m, 2H, Ar−C*H*Me$_2$), 2.37 (s, 6H, N═CMe), 1.17 (d, 12H, Ar−CH*Me$_2$*). Anal. Calcd for C$_{33}$H$_{43}$N$_3$: C, 81.57; H, 7.86; N, 10.57. Found: C, 81.58; H, 7.90; N, 10.45. **3**: ^{1}H NMR (CDCl$_3$): δ 8.44 (d, 2H, Py−Hm), 7.90 (t, 1H, Py−Hp), 7.11 (d, 2H, Ar−Hm), 7.02 (d, 4H, Ar−Hm), 2.40−2.34 (q, 8H, Ar−C*H$_2$*Me), 2.23 (s, 6H, N═CMe), 1.13 (t, 12H, Ar−CH$_2$*Me*). Anal. Calcd for C$_{29}$H$_{35}$N$_3$: C, 81.84; H, 8.29; N, 9.87. Found: C, 81.72; H, 8.36; N, 9.84. **4**: ^{1}H NMR (CDCl$_3$): δ 8.45 (d, 2H, Py−Hm), 7.88 (t, 1H, Py−Hp), 6.88 (m, 4H, Ar−Hm), 2.24 (s, 6H, Ar−Me), 2.38 (s, 6H, N═CMe), 1.99 (s, 12H, Ar−Me). Anal. Calcd for C$_{27}$H$_{31}$N$_3$: C, 81.57; H, 7.86; N, 10.57. Found: C, 81.24; H, 7.76; N, 10.53.

Synthesis of 2,6-Bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine−MoCl$_3$ (5). A THF solution (45 mL) of 2,6-bis[1(2,6-diisopropylphenylimino)ethyl]pyridine (**1**) (0.22 g, 0.51 mmol) was added dropwise to a solution of MoCl$_3$(THF)$_3$ in THF (30 mL) at 0 °C. After the reaction mixture was refluxed for 12 h to give a blue solution, the resulting solution was concentrated and cooled to −25 °C to induce the crystallization generating dark blue crystals of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine−MoCl$_3$ in 25% yield. Anal.

Calcd for $C_{33}H_{43}N_3MoCl_3$: C, 57.93; H, 6.34; N, 6.15. Found: C, 57.62; H, 6.67; N, 6.08; mp > 250 °C. EI-MS (relative ratio) for $C_{33}H_{43}N_3{}^{98}Mo^{35}Cl_3$, *m/z* (relative ratio): 679 (M^+−Cl,2), 646 (M^+−Cl,83), 482 ($C_{33}H_{43}N_3$, 100). ^{1}H NMR spectrum of **5** showed very broadened pattern because of the paramagnetic nature of the resulting Mo(III) species.

Synthesis of 2,6-Bis[1-(2-isopropylphenylimino)ethyl]pyridine−MoCl$_3$ (6). A THF solution (45 mL) of 2,6-bis[1(2-isopropylphenylimino)ethyl]pyridine (**2**) (0.76 g, 1.93 mmol) was added dropwise to a solution of $MoCl_3(THF)_3$ (0.80 g, 1.93 mmol) in THF (45 mL) at 0 °C. After the reaction mixture was refluxed for 12 h to give a blue solution, the resulting solution was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2 to give 2,6-bis[1-(2-diisopropylphenylimino)ethyl]pyridine−MoCl$_3$ in 39% yield as dark blue crystals. Anal. Calcd for $C_{27}H_{31}N_3MoCl_3$: C, 54.06; H, 5.21; N, 7.00. Found: C, 53.28; H, 5.51; N, 6.87; mp > 250 °C. EI-MS for $C_{27}H_{31}N_3{}^{98}Mo^{35}Cl_3$: *m/z* 594 ($M^+$, 3), 561 ($M^+$−Cl, 67), 398 ($C_{27}H_{31}N_3$, 100).

Synthesis of 2,6-Bis[1-(2,6-diethylphenylimino)ethyl]pyridine−MoCl$_3$ (7). A THF solution (60 mL) of 2,6-bis[1(2,6-diethylphenylimino)ethyl]pyridine (**3**) (1.22 g, 2.90 mmol) was dropwise added to a solution of $MoCl_3(THF)_3$ (1.21 g, 2.90 mmol) in THF (30 mL) at 0 °C. After the reaction mixture was refluxed for 12 h to give a blue solution, the resulting solution was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2 to give 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine−MoCl$_3$ in 20% yield as dark blue crystals. Anal. Calcd for $C_{29}H_{35}N_3MoCl_3$: C, 55.47; H, 5.62; N, 6.69. Found: C, 55.40; H, 5.58; N, 6.53; mp > 250 °C. EI-MS: *m/z* 621 (M^+, 2), 588 (M^+−Cl, 92), 424 ($C_{29}H_{35}N_3$, 100).

Synthesis of 2,6-Bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine−MoCl$_3$ (8). A THF solution (30 mL) of 2,6-bis[1(2,4,6-trimethylphenylimino)ethyl]pyridine (**4**) (0.94 g, 2.39 mmol) was dropwise added to a solution of $MoCl_3(THF)_3$ (1.0 g, 2.39 mmol) in THF (30 mL) at 0 °C. After the reaction mixture was refluxed for 12 h to give a blue solution, the resulting solution was concentrated and cooled to to −25 °C to induce dark blue crystals of 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine−MoCl$_3$ in 23% yield as dark blue crystals. Anal. Calcd for $C_{27}H_{31}N_3MoCl_3$: C, 54.06; H, 5.21; N, 7.00. Found: C, 54.01; H, 5.15; N, 6.89; mp > 250 °C. EI-MS for $C_{27}H_{31}N_3{}^{98}Mo^{35}Cl_3$: *m/z* 594 ($M^+$, 4), 561 ($M^+$−Cl, 75), 398 ($C_{27}H_{31}N_3$, 100).

Synthesis of Terpyridine−MoCl$_3$ (9). To a solution of $MoCl_3(THF)_3$ (0.37 g, 0.84 mmol) in THF (45 mL) was added dropwise a solution of 2,2′:6′,2″-terpyridine (0.20 g, 0.84 mmol) in THF (30 mL) at 0 °C. The reaction mixture was refluxed for 3 h, resulting in the formation of purple suspension. The precipitates were washed with THF and hexane, and dried in vacuo, to give terpyridine−MoCl$_3$ (**9**) as purple powder in 93% yield (0.34 g). Anal. Calcd for $C_{15}H_{11}N_3MoCl_3$: C, 37.94; H, 2.69; N, 10.21. Found: C, 37.98; H, 2.72; N, 10.01; mp > 250 °C. EI-MS for $C_{15}H_{11}N_3{}^{98}Mo^{35}Cl_3$: *m/z* 406 ($M^+$, 4), 373 ($M^+$−Cl, 15), 209 ($C_{15}H_{11}N_3$, 100).

Ring Opening Metathesis Polymerization of Norbornene with Molybdenum Complex/MMAO System. To a solution of a Mo complex (0.02 mmol) in dry toluene (0.5 mL) was added MMAO (300 equiv of Mo complex, 6 mmol), and the mixture was heated to 60 °C for 5 min. A norbornene solution (400 equiv, 4 mmol) in toluene (0.5 mL) was added to the reaction mixture and stirred there for a fixed time at a fixed temperature. The resulting polymer was quenched with a large amount of methanol containing 2 mol % of concentrated HCl aqueous solution. The polymer structure, molecular weights, and the thermal properties were analyzed by NMR, GPC, and DSC.

Ethylene Polymerization with Mo Complex/MMAO System. To a Mo complex (0.01 mmol) in dry toluene (0.5 mL) was added MMAO (5 mmol). The mixture was stirred for 5 min at 60 °C, then the system was evacuated at −78 °C, and ethylene was introduced with Schlenk techniques from a balloon containing ethylene. The polymerization was carried out at 25 °C for 20 min. The resulting polymer was quenched with excess methanol containing a small amount of hydrochloric acid. The polymer structure, molecular weights, and the thermal properties were analyzed by NMR, GPC, and DSC.

Table 8. Crystal Data and Data Collections for 6

chem form	$C_{30}H_{37}N_3MoCl_3$	F_{000}	1460.00
formula wt	712.85	μMo Kα/cm^{-1}	8.03
color	black, needle	temp/°C	23
cryst dimens	0.50 × 0.25 × 0.30	scan type	$\omega-2\theta$
cryst system	monoclinic	$2\theta_{max}$	54.9
lattice param	no. of reflections	6846	
a/Å	14.258(4)	struct solution	direct method
b/Å	13.799(7)	refinement	full-matrix least-squares
c/Å	17.402(3)	no. of observation	2206
β	97.98(2)	no. of variables	337
V/Å^3	3390(2)	GOF	1.50
space group	$P2_{1/C}$(#14)	R	0.083
Z	4	R_w	0.084
D_{calcd}/g cm^{-3}	1.396		

2 copolymerization of ethylene with norbornene was carried out using the following procedure. To a solution of a Mo complex (0.02 mmol) in dry toluene (0.5 mL) was added MMAO (500 equiv of a Mo complex, 10 mmol), and the mixture was heated to 25 °C for 5 min. Ethylene was bubbled into the solution (40 mL/min) through a glass capillary for a fixed time, and the mixture was stirred there for 20 min. Then phenylacetylene or 1,4-diphenylbutadiyne (0.02 mmol) was added and stirred there for 10 min. Then norbornene (300 equiv, 6 mmol) in toluene (0.5 mL) was added to the reaction mixture. After stirring the mixture for 12 h at 25 °C, the resulting system was quenched with excess methanol.

Dicyclopentadiene Polymerizations with 5/MMAO System. To a solution of a Mo complex (0.02 mmol) in dry toluene (0.5 mL) was added MMAO (100 equiv of Mo complex, 2 mmol), and the mixture was heated to 60 °C for 3 h. A *endo*-dicyclopentadiene solution (100 equiv, 2 mmol) in toluene (0.5 mL) was added to the reaction mixture and stirred there for 3 h at 60 °C. The resulting polymer was quenched with a large amount of methanol containing 2 mol % of hydrochloric acid. Hydrogenation of the resulting polymer was carried out as follows. Poly(dicyclopentadiene) (1.3 g, 10 mmol) was dispersed in cyclohexane (30 mL) containing $(Cy_3P)_2RuCl{=}CHPh$ (0.01 mmol), and hydrogenation was performed at 160 °C for 8 h at 1.0 MPa of H_2. A 100% hydrogenation was achieved. The resulting polymer was treated with methanol (30 mL) containing 2 mol % of HCl aqueous solution and then dried in vacuo.

X-ray Structure Determination. A black needle single crystal of **7** was sealed in a glass capillary under argon. The X-ray data for **7** were collected at 23 °C on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation. No empirical absorption correction was applied. The basic crystallographic parameters are listed in Table 8. Cell constants and the orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25°, carefully centered reflections in the range 23.41° < 2θ < 28.77° correspond to a primitive monoclinic cell with dimensions. The standard reflections were monitored at every 150 reflections and did not show any significant change. The structures were solved by the direct method and expanded using Fourier techniques. Some non-hydrogen atoms were anisotropically refined, while the rest were isotropically refined. Hydrogen atoms were included but not refined. All the calculations were performed by the use of teXsan crystallographic software package.

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Supporting Information Available: Crystallographic data for the structural analysis of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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