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Dinuclear Metallocenes with a Modulated Biphenylene Bridge for Olefin Polymerization

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Dinuclear group 4 metallocene catalysts linked by a biphenylene or 1,2-diphenylethylene bridge, namely $[4,4'\text{-}(C_5Me_4)_2\text{-}(C_6H_4)_2][CpZrCl_2]_2$ (**2a**), $[p\text{-}(C_5Me_4)C_6H_4CH_2]_2[CpZrCl_2]_2$ (**2b**), $[p\text{-}(3,4\text{-}Me_2C_5H_2)C_6H_4CH_2]_2[CpZrCl_2]_2$ (**2c**), $[(C_5Me_4)_2\text{-}(C_6H_4)_2][TiCl_3]_2$ (**3a**), $[p\text{-}(C_5Me_4)C_6H_4CH_2]_2[TiCl_3]_2$ (**3b**), and $[p\text{-}(3,4\text{-}Me_2C_5H_2)C_6H_4CH_2]_2[TiCl_3]_2$ (**3c**), have been prepared and the crystal structures of **2b** and **3b** determined by X-ray diffraction methods. The crystal structures reveal that these complexes consist of two equivalent metal units inverted with respect to the center of the bridge. All the complexes were tested for the polymerization of ethylene and styrene in the presence of methylaluminoxane (MAO), and direct comparisons of their catalytic properties with those of the corresponding mononuclear analogues $[(PhC_5Me_4)\text{-}CpZrCl_2]$ (**4a**), $[(p\text{-}TolC_5Me_4)CpZrCl_2]$ (**4b**), $[(1\text{-}p\text{-}Tol\text{-}3,4\text{-}Me_2C_5H_2)CpZrCl_2]$ (**4c**), $[(PhC_5Me_4)TiCl_3]$ (**5a**), $[(p\text{-}TolC_5Me_4)TiCl_3]$ (**5b**), and $[(1\text{-}p\text{-}Tol\text{-}3,4\text{-}Me_2C_5H_2)TiCl_3]$ (**5c**) were performed. The dinuclear zirconocenes show a high activity in ethylene polymerization comparable with those of the corresponding mononuclear catalysts and give an increased molecular weight of polyethylene. The dinuclear half-sandwich titanocenes exhibit similar or slightly lower activity and molecular weight in styrene polymerization compared with their mononuclear analogues.

Introduction

Single-site catalytic systems for olefin polymerization based on group 4 metal complexes have become well established during the last two decades and have provided various opportunities to tailor the polymer properties, especially molecular weight, molecular weight distribution, and stereochemistry, as well as high catalytic activity.[1–6] The fruits of these endeavors are the various kinds of catalyst systems that are now being used in practical applications. Syndiotactic polystyrene (sPS) from half-sandwich metallocene catalysts and linear low-density polyethylene (LLDPE) from constrained-geometry catalysts are typical products available commercially from single-site catalyst systems. Most of these catalyst systems, however, involve mononuclear complexes, as dinuclear systems that consist of two active centers linked within the same molecule have become a focus of attention only since the first report by Mülhaupt et al.[7] on a phenylene-bridged dinuclear zirconocene system for propylene polymerization. Initial efforts made by several groups have shown that these catalyst systems are effective in olefin polymerization[8–11] but they have still remained much less defined in terms of structural aspects, class of catalysts, and kinds of polymerization they can perform in comparison with the well-known mononuclear systems.

Recently, it has been found that dinuclear systems are able to show interesting catalytic behaviors that are different from those of mononuclear systems. Systematic polymerization studies by Noh et al. using polysiloxane- and polymethylene-bridged dinuclear complexes have demonstrated that the catalytic activity[12,13] and co-monomer incorporation ratio[14–16] are strongly correlated with both the nature and the length of the bridging group employed. Marks et al. have revealed that dinuclear constrained-geometry catalysts connected by ethylene and/or methylene bridges exhibit unique polymerization behaviors such as high α-olefin incorporation,[17,18] high activity in styrene polymerization,[19] and branched or significantly increased molecular weights in ethylene polymerization[18,20–22] mainly due to the cooperative interactions between two active centers. Alt et al. have also reported asymmetric dinuclear zirconocenes that are capable of producing polyethylene with a bimodal molecular weight distribution.[23,24]

Although it has been suggested from the foregoing studies that the catalytic properties of dinuclear complexes can be strongly affected by the nature of the bridging group and possible cooperative metal–metal interactions, very few studies on the variation of the bridging group have been

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performed. Flexible alkylene groups still constitute the majority of bridges,[7–26] therefore it is of great value to examine the electronic and/or steric effects of the bridging group that play an important role in governing the catalytic properties of dinuclear complexes and thereby rationalize the cooperative reactivity of dinuclear catalysts. In this regard, our group recently reported the well-defined dinuclear group 4 metal complexes $[4,4'-(C_5Me_4)_2(C_6H_4)_2][CpZrCl_2]_2$ (**2a**) and $[4,4'-(C_5Me_4)_2(C_6H_4)_2][TiCl_3]_2$ (**3a**), which are linked by a rigid biphenylene bridge, and the direct comparison of their catalytic properties with those of the corresponding mononuclear analogues in ethylene and styrene polymerization.[27] We observed an increase of both molecular weight of polymer and catalytic activity, irrespective of the co-catalyst employed, especially in ethylene polymerization.

In the present report, which includes a further investigation of the polymerization behavior of the biphenylene-bridged system, we aim to endow the existing biphenylene group with flexibility that could provide additional metal–metal interactions and at the same time to keep each metal center highly active by minimizing the steric hindrance between the two active centers. To this end, we have developed novel dinuclear group 4 catalysts containing bis(cyclopentadienido) ligands bound to a rigid but flexible 1,2-diphenylethylene bridge. A complete set of comparative polymerization studies in olefin polymerization with the corresponding mononuclear catalysts is also reported.

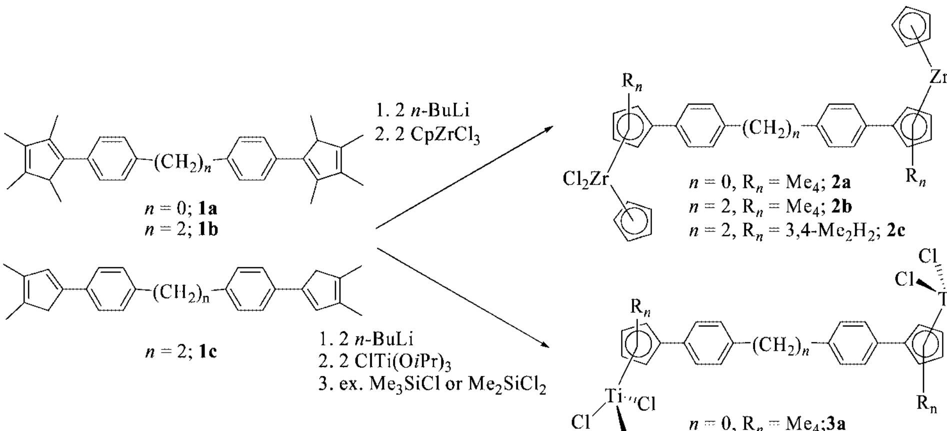
Results and Discussion

Complexes Synthesis and Characterization

Two new ligands (**1b** and **1c**) were synthesized by a procedure analogous to that for ligand **1a** reported in our previous communication.[27] These ligands are poorly soluble in common organic solvents but are more soluble than **1a**, thus reflecting their flexible nature. The zirconium complexes **2b** and **2c** were prepared in a straightforward manner by the direct transmetalation of dilithium salts of the ligands with two equivalents of $[CpZrCl_3]$ in thf. Complexes **2b** and **2c** have much better solubility then **1a** in hydrocarbon solvents, which could be an important advantage when the immobilization of the catalysts is considered for industrial applications. Reaction of the dilithium salt of the ligands with two equivalents of $ClTi(O\textit{i}Pr)_3$ in thf, followed by in situ chlorination with an excess of Me_3SiCl or Me_2SiCl_2 in CH_2Cl_2, also afforded the final titanium trichloride complexes **3b** and **3c** (Scheme 1). Complex **3c** is less soluble in $CHCl_3$ and CH_2Cl_2 than **3a** and **3b**, which suggests that the sterically less congested nature of **3c** allows the retention of planarity between the phenyl and cyclopentadienido rings in the ligand backbone. Two singlets for the methyl proton resonance in the ^1H NMR spectra of **2a**, **2b** and **3a**, **3b**, and one singlet methyl resonance for **2c** and **3c** indicate that the two metal units in these dinuclear complexes are in an identical chemical environment in solution.

X-ray Crystallographic Structures of 2b and 3b

The molecular structures of **2b** and **3b** are depicted in Figure 1 and selected interatomic distances and angles are listed in Table 1. The zirconium complex **2b** crystallizes in the space group *C*2/*c* with only one half of the molecule in the asymmetric unit. Interestingly, the diphenylethylene bridge adopts a *gauche* conformation in which the molecule has a C_2-symmetric axis perpendicular to the C(16)–C(16′) bond. Thus, two $[Cp'CpZrCl_2]$ ($Cp' = C_5Me_4Ph$) fragments are perfectly inverted along the rotation axis, which indicates that complex **2b** consists of two equivalent units in the solid state. The detailed structural analysis indicates that the bonding geometry around the zirconium center, such as the Cl(1)–Zr–Cl(2) and Cg(1)–Zr–Cg(2) bond angles and Zr–Cl and Zr–Cg bond lengths shown in Table 1, are in a similar range to those of mononuclear, unbridged zirconocene complexes.[28–30] The dihedral angle of 41.28(18)° between the C_5Me_4 ring [Cp(1)] and the adjacent phenylene ring [Ph(1)] is closer to that of the phenyl-substituted mo-



Scheme 1.

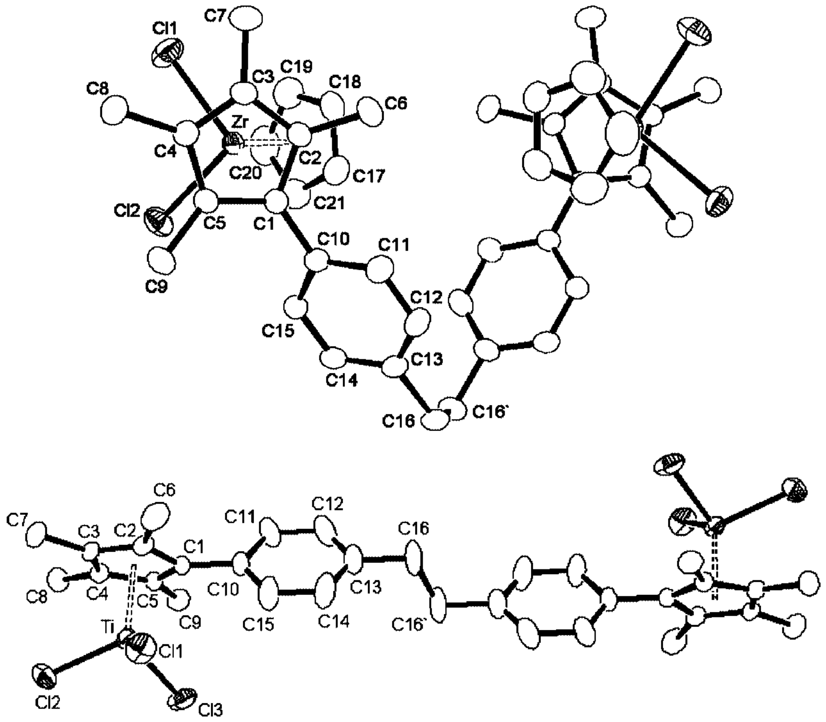


Figure 1. Molecular structures of **2b** (top) and **3b** (bottom).

nonuclear zirconocene **4a** (47.2°)[31] than that observed in the biphenylene-bridged **2a** [63.6(2)°],[27] which suggests that flexible nature of the bridging group makes the steric environment of each metallocene unit of **2b** similar to that of the mononuclear **4a**.

Table 1. Selected bond lengths [Å] and angles [°] for **2b** and **3b**.

Compound	**2a** (M = Zr)[a]	**2b** (M = Zr)	**3b** (M = Ti)
Cl(1)–M–Cl(2)	96.5(0)	97.07(3)	103.57(11)
Cg(1)–M–Cg(2)[b]	129.8	130.98	–
Cp′(1)–Ph(1)[c]	63.6(2)	41.28(18)	62.6(3)
M–Cl(1)	2.429(1)	2.4337(11)	2.242(4)
M–Cl(2)	2.440(1)	2.467(10)	2.245(4)
M–Cl(3)	–	–	2.240(4)
M–Cg(1)	2.224(1)	2.2231(15)	2.026(4)
M–Cg(2)	2.199(2)	2.213(2)	–

[a] Data taken from ref.[27] [b] Cg(1) and Cg(2) are the centroids of the C_5Me_4 (C1–C5) and Cp (C21–C25) rings, respectively. [c] Cp′(1) is the plane of C_5Me_4 (C1–C5) and Ph(1) the plane of C_6H_4 (C10–C15).

The titanium complex **3b** crystallizes in the space group *C*2/*c* and contains half of each of two independent molecules in the asymmetric unit. Similarly to **2a** and **3a**, two Cp′TiCl$_3$ (Cp′ = C_5Me_4Ph) fragments are also perfectly inverted with respect to the C(16)–C(16′) bond axis, thus indicating that complex **3b** consists of two equivalent units in the solid state. According to the solid-state structure, **3b** adopts an *anti* conformation of the diphenylethylene bridge. The bond angles and distances around titanium are also similar to those for mononuclear complexes but, interestingly, the dihedral angle between the C_5Me_4 ring [Cp(1)] and the adjacent phenylene ring [Ph(1)] is much larger [62.6(3)°] than those of the corresponding dinuclear zirconocene **2b** [41.28(18)°] and [($C_6H_4C_5Me_4$)TiCl$_2$]$_2$(μ-O) (50.4°).[32]

Ethylene Polymerization

Ethylene polymerizations with the dinuclear zirconocene complexes **2a**–**c** were carried out in toluene solution under 1 bar of ethylene. To compare their catalytic properties with those of the corresponding mononuclear catalysts, polymerizations with **4a**–**c** were also performed under identical conditions (Table 2). All the catalysts show high activities that are in a range similar to that of the corresponding mononuclear complexes **4a**–**c** at all reaction temperatures. The polyethylenes produced by the dinuclear zirconocenes also show a narrow molecular weight distribution (M_w/M_n) similar to that of polyethylenes obtained with the mononuclear complexes, which suggests that the two zirconium centers in the dinuclear complexes behave as independent single active sites, as expected from the crystal structures and NMR spectra. In particular, biphenylene-bridged **2a** shows higher activity than mononuclear **4a** at high temperature, while diphenylethylene-bridged **2b** and **2c** show lower activity than mononuclear **4b** and **4c** at the low- and high-temperature limits. Thus, an enhanced thermal stability of the active species is seen only for biphenylene-bridged **2a** among the three dinuclear systems. Moreover, the activity of **2a** is higher than that of **2b** at all temperatures, while the corresponding mononuclear analogues **4a** and **4b** exhibit a similar activity. In addition, in the case of the flexible diphenylethylene-bridged systems, a higher activity was observed for di-

Table 2. Ethylene polymerization results with catalysts **2a**–**c** and **4a**–**c**.[a]

Entry	Cat. [μmol]	T_p [°C]	Yield [g]	A ($\times 10^{-3}$)[b]	M_w ($\times 10^{-3}$)	M_w/M_n	T_m [°C]
1	**2a** (1.0)	30	0.628	9.42	732	1.97	131.9
2	**2a** (1.0)	50	0.631	9.47	392	2.23	135.1
3	**2a** (1.0)	70	1.035	15.53	135	1.96	134.0
4	**2a** (1.0)	90	0.548	8.22	54	2.02	133.3
5	**4a** (1.0)	30	0.615	9.23	534	2.10	135.7
6	**4a** (2.0)	50	0.782	11.73	317	2.28	134.9
7	**4a** (2.0)	70	0.633	9.50	121	2.14	134.5
8	**4a** (2.0)	90	0.426	6.39	67	2.54	132.9
9	**2b** (1.0)	30	0.383	5.75	821	1.93	131.2
10	**2b** (1.0)	50	0.556	8.34	525	2.31	133.7
11	**2b** (1.0)	70	0.935	14.03	230	2.2	134.1
12	**2b** (1.0)	90	0.238	3.57	88	2.72	133.8
13	**4b** (2.0)	30	0.545	8.18	413	2.02	136.8
14	**4b** (2.0)	50	0.582	8.73	298	2.87	135.8
15	**4b** (2.0)	70	0.850	12.75	222	3.85	133.8
16	**4b** (2.0)	90	0.451	6.77	73	3.22	134.2
17	**2c** (1.0)	30	0.496	7.44	654	2.21	135.7
18	**2c** (1.0)	50	0.798	11.97	334	2.57	135.4
19	**2c** (1.0)	70	0.897	13.46	114	2.90	133.2
20	**2c** (1.0)	90	0.546	8.19	47	2.99	131.6
21	**4c** (2.0)	30	0.690	10.35	552	2.39	136.0
22	**4c** (2.0)	50	0.714	10.71	267	2.92	135.8
23	**4c** (2.0)	70	1.026	15.39	147	3.65	134.3
24	**4c** (2.0)	90	0.560	8.40	59	3.97	131.8
25	Cp_2ZrCl_2 (2.0)	50	0.571	8.57	235	2.92	134.7

[a] Conditions: P(ethylene): 1 bar; solvent: 50 mL of toluene; t_p: 2.0 min; MAO: s-MAO; [Al]/[Zr]: 1000. [b] Activity: kg of PE per mol of Zr per hour per bar.

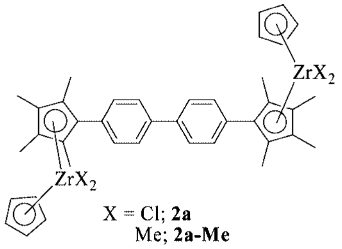
methyl-substituted **2c** than for tetramethyl-substituted **2b**, which implies that the steric effect of the ligand strongly influences the activity. These results may indicate that the lower steric hindrance and the possible electronic stabilization caused by the rigid and conjugative nature of the biphenylene bridge in **2a** lead to the higher activity.

Thus, it can be suggested that the biphenylene group acts as a much more effective bridge in terms of catalytic activity. Noh et al. have pointed out that the more electron releasing and the longer the bridge, the higher the activity of the dinuclear zirconium complexes compared with that of the mononuclear catalyst in ethylene polymerization.[13] In our case, the rigidity, coupled with the appropriate length of the bridging unit, provides favorable electronic stabilization and steric effects and thus likely plays an important role in governing catalytic activity when compared with the flexible diphenylethylene-bridged systems.

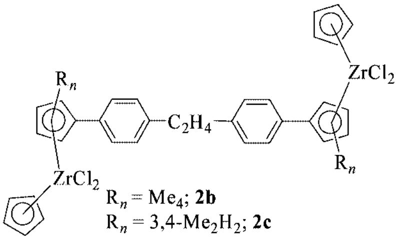
The characteristic most noteworthy of mention is the molecular weight of the polyethylene: the polyethylenes produced by **2a**–**c** have a higher molecular weight than those of **4a**–**c**, especially at temperatures below 50 °C, while at high temperature (>70 °C), the values are similar to those of the mononuclear analogues. Between two diphenylethylene-bridged systems, the more electron-releasing **2b** gives higher molecular weights than **2c** at all temperatures, as expected. However, in contrast to the trend in activity, the molecular weight given by **2b** is greater than the biphenylene-bridged **2a** under identical conditions. Note that the ratio of molecular weights between **2b** and **4b** is about 2.0 while that between **2a** and **4a** is about 1.5 (Figure 2). This result can be mainly explained by steric reasons, as for the activity. Due to the flexible nature of the bridge, the two metal centers in **2b** can exert mutual steric hindrance by being located in proximal positions despite the partial relief of such an interaction due to the presence of an additional phenylene linkage. This increased steric hindrance towards the growing polymer chains presumably leads to a reduced rate of chain-transfer reactions.[33] This assumption also appears to be valid for the higher molecular weight produced by **2b** and **2c** in comparison to mononuclear **4b** and **4c**, respectively.

Styrene Polymerization

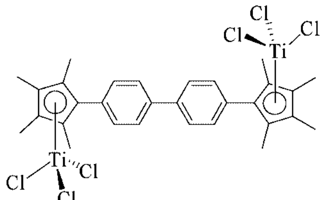
From the polymerization results in Table 3, it can be seen that dinuclear half-sandwich titanocenes behave as highly active, single-site catalysts for styrene polymerization, and the syndiotactic index (SI) and melting temperature (T_m) of the polystyrenes suggest that the syndiospecific stereocontrol is also well maintained. For a given Cp ligand, a biphenylene bridge appears to form a more efficient dinuclear catalytic system than a diphenylethylene bridge, as judged from the polymerization behavior of **3a** and **3b** at all temperatures (note the higher activity of biphenylene-bridged **3a** than diphenylethylene-bridged **3b** and the retention of the high activity of **3a** even at 90 °C). For a given bridging ligand, the sterically less congested dimethyl-substituted Cp ligand fragment affords a catalytically more active system than the tetramethyl-substituted Cp ligand fragment, as exemplified by **3b** and **3c**. A similar effect of the Cp ligand on the catalytic system has been observed with **5c** and **5b** and other reported mononuclear catalyst systems.[34–36]



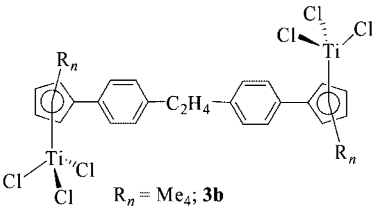
X = Cl; **2a**
Me; **2a-Me**



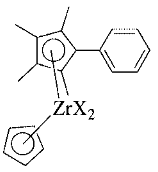
R_n = Me_4; **2b**
R_n = 3,4-Me_2H_2; **2c**



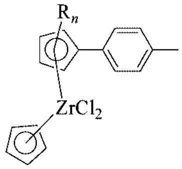
3a



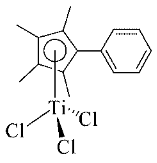
R_n = Me_4; **3b**
R_n = 3,4-Me_2H_2; **3c**



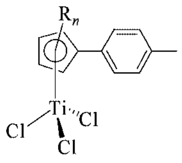
X = Cl; **4a**
Me; **4a-Me**



R_n = Me_4; **4b**
R_n = 3,4-Me_2H_2; **4c**



5a



R_n = Me_4; **5b**
R_n = 3,4-Me_2H_2; **5c**

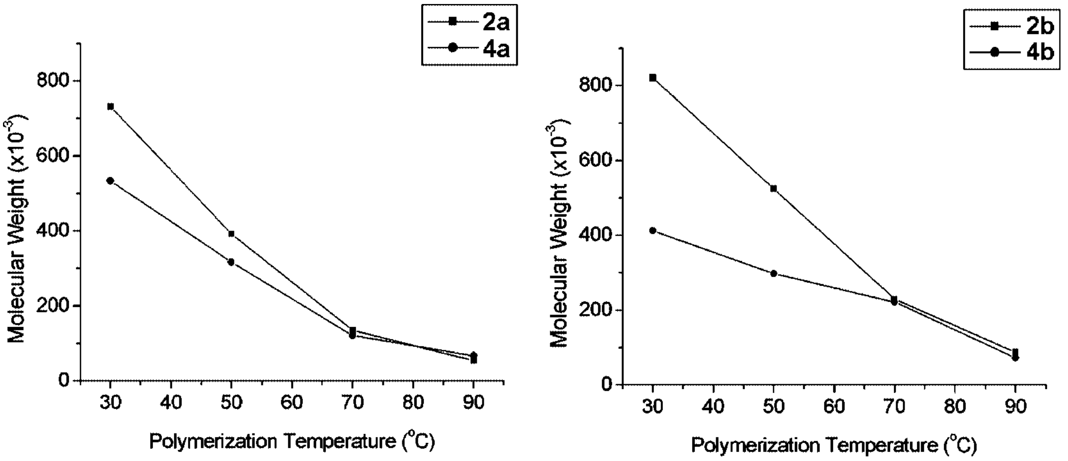


Figure 2. Molecular weight difference between the polymers obtained with **2a** and **4a** (left) and **2b** and **4b** (right).

The activities of the dinuclear complexes are slightly lower than those of the corresponding mononuclear systems. The extent of the activity decrease is more significant in **3b** and **3c**, which have a flexible diphenylethylene bridge, than in **3a**, which has a rigid biphenylene bridge, thereby indicating the effect of the steric influence on the catalytic activity in styrene polymerization.[37] Rausch et al. have also reported that ethylene-bridged dinuclear indenyltitanium trichloride shows much lower activity than the corresponding mononuclear compound in spite of similar syndioselectivity of these two complexes.[38] This result may imply that the bridge flexibility in **3b** and **3c** makes the two polymer chains growing at the two active centers exert a steric influence on each other which slows down the rate of chain propagation.[39]

The polystyrenes produced by dinuclear **3a**–**c** have a lower molecular weight than those of the corresponding mononuclear **5a**–**c** at all reaction temperatures. This can be explained in terms of the steric effect of the ligand, which means that β-H elimination becomes preferred to propagation as the steric hindrance between the polymer chain and ligand in half-sandwich metallocenes increases.[39] However, in contrast to the activity trend, the molecular weights of the polymers formed by the dinuclear systems are in the order **3a** > **3b** > **3c**, which is similar to the order of the mononuclear systems (**5a** ≈ **5b** > **5c**). The low molecular

Table 3. Styrene polymerization results with catalysts **3a**–**3c** and **5a**–**5c**.[a]

Entry	Cat. [μmol]	T_p [°C]	Yield [g]	Activity[b]	M_w ($\times10^{-3}$)	M_w/M_n	T_m [°C]	SI [%][c]
1	**3a** (5.0)	50	1.334	400.2	297	1.99	267	93
2	**3a** (5.0)	70	1.694	508.2	214	1.81	267	96
3	**3a** (5.0)	90	1.636	490.8	98.7	1.91	272	95
4	**5a** (10.0)	50	1.153	345.9	460	1.82	268	93
5	**5a** (10.0)	70	1.996	598.8	246	1.95	268	99
6	**5a** (10.0)	90	1.872	561.6	151	1.88	268	95
7	**3b** (5.0)	50	1.055	316.5	267	1.77	268	98
8	**3b** (5.0)	70	1.694	508.2	182	1.77	269	93
9	**3b** (5.0)	90	1.400	420.0	93.8	1.92	271	95
10	**5b** (10.0)	50	1.192	357.6	420	1.86	269	92
11	**5b** (10.0)	70	2.671	801.3	269	2.03	272	96
12	**5b** (10.0)	90	2.565	769.5	139	1.92	272	97
13	**3c** (5.0)	50	1.640	492.0	279	1.94	268	95
14	**3c** (5.0)	70	2.804	851.2	119	2.05	270	97
15	**3c** (5.0)	90	2.119	635.7	57.9	1.92	268	96
16	**5c** (10.0)	50	2.672	801.6	347	2.01	271	96
17	**5c** (10.0)	70	3.256	976.8	147	2.02	270	98
18	**5c** (10.0)	90	3.083	924.9	58.5	1.91	266	96
19	Cp*TiCl$_3$	50	0.963	288.9	310	1.90	266	96

[a] Conditions: solvent: 50 mL of toluene; [Al]/[Ti]: 1000; styrene: 5.0 mL; t_p: 20 min; MAO: s-MAO. [b] Activity: kg of PS per mol of Ti per hour. [c] Syndiotacticity determined from the amount of polymer insoluble in 2-butanone.

weight obtained with both the most active complexes (**3c** and **5c**) appears to be mainly ascribed to the lower electron-donating effect of the dimethyl-substituted ligand. The molecular weight trend **3a** > **3b** can be considered to be a manifestation of the reduced steric effects in **3a** compared to **3b**.

Conclusions

The biphenylene- and diphenylethylene-bridged dinuclear zirconocenes [4,4′-(C$_5$Me$_4$)$_2$(C$_6$H$_4$)$_2$][CpZrCl$_2$]$_2$ (**2a**), [*p*-(C$_5$Me$_4$)C$_6$H$_4$CH$_2$]$_2$[CpZrCl$_2$]$_2$ (**2b**), and [*p*-(3,4-Me$_2$C$_5$H$_2$)C$_6$H$_4$CH$_2$]$_2$[CpZrCl$_2$]$_2$ (**2c**) consistently provide high molecular weight polymers and have a high catalyst activity in ethylene polymerization, although there are some differences, including both structural and polymerization properties, between rigid and flexible bridged dinuclear complexes in terms of activity and molecular weight trends. In contrast, the corresponding dinuclear half-sandwich titanocenes [(C$_5$Me$_4$)$_2$(C$_6$H$_4$)$_2$][TiCl$_3$]$_2$ (**3a**), [*p*-(C$_5$Me$_4$)C$_6$H$_4$CH$_2$]$_2$[TiCl$_3$]$_2$ (**3b**), and [*p*-(3,4-Me$_2$C$_5$H$_2$)C$_6$H$_4$CH$_2$]$_2$[TiCl$_3$]$_2$ (**3c**) do not show any enhanced polymerization properties in styrene polymerization compared to their mononuclear analogues. Indeed, they show a significant decrease in the molecular weight of the polymer produced and a slight decrease of catalytic activity. These results appear to be due to the cooperative participation of the electronic effect of the two cationic metal centers through the biphenylene or diphenylethylene bridge and/or the steric effects between them.

Experimental Section

General: Tetrahydrofuran, toluene, *n*-hexane, and *n*-pentane were distilled from Na-K alloy, Et$_2$O from Na-benzophenone ketyl, and CH$_2$Cl$_2$ from CaH$_2$. All solvents were stored over activated molecular sieves (5 Å). All other chemicals were used without any further purification. 3,4-Dimethylcyclopent-2-enone,[40] 4,4′-(C$_6$H$_4$)$_2$-(C$_5$Me$_4$H)$_2$ (**1a**),[27] (*p*-BrC$_6$H$_4$CH$_2$)$_2$,[41] [4,4′-(C$_5$Me$_4$)$_2$(C$_6$H$_4$)$_2$]-[CpZrCl$_2$]$_2$ (**2a**),[27] [4,4′-(C$_5$Me$_4$)$_2$(C$_6$H$_4$)$_2$][TiCl$_3$]$_2$ (**3a**),[27] [(PhC$_5$Me$_4$)CpZrCl$_2$] (**4a**),[31] [(*p*-tolylC$_5$Me$_4$)CpZrCl$_2$] (**4b**),[31] 1-tolyl-3,4-Me$_2$C$_5$H$_3$,[7] [(1-tolyl-3,4-Me$_2$C$_5$H$_2$)CpZrCl$_2$] (**4c**),[7] [(PhC$_5$Me$_4$)TiCl$_3$] (**5a**),[42] and [(*p*-tolylC$_5$Me$_4$)TiCl$_3$] (**5b**)[43] were prepared according to literature procedures. Methylaluminoxane (MAO) was used as a solid (s-MAO). This was obtained by complete evaporation of the solvent and residual AlMe$_3$ from a toluene solution of PMAO (Witco, EUROCEN 30T) and a toluene solution of PMAO (Witco, EUROCEN 10T). Polymerization-grade ethylene monomer from Honam Petrochemical Corporation was used after purification by passing through Labclear™ and Oxiclear™ filters. Styrene monomer purchased from Aldrich was used after purification by passing through an alumina column. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Spectropin 400 spectrometer at ambient temperature. All chemical shifts are reported in δ units with reference to the residual peaks of CDCl$_3$ for proton (δ = 7.24 ppm) and carbon (δ = 77.0 ppm). Elemental analyses were carried out with an EA 1110-FISONS (CE Instruments) at KAIST.

Synthesis of [*p*-(C$_5$Me$_4$H)C$_6$H$_4$CH$_2$]$_2$ (1b): A solution of (*p*-BrC$_6$H$_4$CH$_2$)$_2$ (3.40 g, 10 mmol) in 50 mL of diethyl ether was treated with 2.2 equiv. of *n*BuLi (8.8 mL) at 0 °C and the reaction mixture was stirred at this temperature for 1 h. The slow formation of a white precipitate was observed and the reaction mixture was then warmed to room temperature and stirred for a further 2 h. The colorless solution was then decanted off and 30 mL of thf was added to the resulting dilithium salt. Subsequently, two equivalents of 2,3,4,5-tetramethylcyclopent-2-enone (2.76 g) in 20 mL of thf was added slowly through a cannula at –78 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight. The resulting light orange solution was treated with 30 mL of a saturated aqueous solution of NH$_4$Cl. The organic portion was separated and the aqueous layer was further extracted with diethyl ether (50 mL). The combined organic portions were dried with anhydrous MgSO$_4$, filtered, and the solvents evaporated to dryness to afford a colorless oily product. The crude product was redissolved in CH$_2$Cl$_2$ (30 mL) and a catalytic amount of solid *p*-TsOH (0.1 g) was added to the solution at room temperature. A yellow solid was immediately formed, and the stirring was continued for a further hour. The volume of the resulting reaction mixture was reduced to 10%, and 30 mL of *n*-hexane was poured into the flask in order to precipitate the product and dissolve the unreacted materials. The large amount of yellow solid obtained was filtered through a glass frit and washed successively with ethanol (30 mL), diethyl ether (30 mL), and *n*-pentane (30 mL). Drying in vacuo afforded 2.83 g of **1b** in 67% yield. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.18 (m, 8 H), 3.17 (q, 2 H), 2.93 (m, 4 H), 2.02 (s, 6 H), 1.91 (s, 6 H), 1.85 (s, 6 H), 0.95 (d, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 142.7, 140.4, 139.0, 136.7, 135.0, 134.8, 128.4, 128.1, 50.1, 37.6, 14.9, 12.7, 11.9, 11.1 ppm. EIMS: *m/z* 422 (85) [M^+], 408 (9) [M^+ – CH_2], 225 (15) [M^+ – $C_6H_4C_5Me_4H$], 211 (100) [$M^+/2$]. $C_{32}H_{38}$ (422.64): calcd. C 90.94, H 9.06; found C 90.33, H 9.44.

Synthesis of [*p*-(3,4-$Me_2C_5H_3$)$C_6H_4CH_2$]$_2$ (1c): An identical procedure to that for the synthesis of **1b** was employed with 3,4-dimethylcyclopent-2-enone (2.18 g) instead of 2,3,4,5-tetramethylcyclopent-2-enone. This afforded 2.31 g of an ivory solid (**1c**) in 63% yield. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.35 (d, 4 H), 7.09 (d, 4 H), 6.60 (s, 2 H), 3.24 (s, 4 H), 2.86 (s, 4 H), 1.96 (s, 6 H), 1.87 (s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 142.4, 139.7, 135.5, 135.4, 134.2, 131.0, 128.6, 124.5, 45.3, 37.6, 13.4, 12.6 ppm. EIMS: *m/z* 366 (76) [M^+], 183 (100) [$M^+/2$], 167 (61) [$M^+/2$ – CH_3]. $C_{28}H_{30}$ (366.54): calcd. C 91.75, H 8.25; found C 91.23, H 8.52.

Synthesis of [{[*p*-(C_5Me_4)$C_6H_4CH_2$][$CpZrCl_2$]}$_2$] (2b): A slurry of **1b** (0.422 g, 1.00 mmol) in 20 mL of thf was treated with two equivalents of *n*BuLi (0.8 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. Two equivalents of [$CpZrCl_3$] (2.0 mmol, 0.525 g) dissolved in 10 mL of thf was added to the resulting yellow suspension through a cannula at –78 °C. The reaction mixture was then warmed to room temperature and stirred for 24 h. The golden-yellow solution formed was then evaporated to dryness and extracted with 30 mL of toluene. The mixture was filtered through a Celite pad, and the light-yellow filtrate was evaporated to dryness. The crude product was washed twice with 10 mL of a mixture of *n*-hexane and diethyl ether (2:1, v/v). Drying in vacuo afforded spectroscopically pure **2b** as a light-yellow solid (0.639 g, 73%). Recrystallization of a concentrated CH_2Cl_2 solution of **2b** layered with *n*-hexane at room temperature afforded light golden colored, single crystals suitable for an X-ray diffraction study. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.19 (d, 4 H), 7.05 (d, 4 H), 6.13 (s, 10 H), 2.99 (s, 4 H), 2.21 (s, 12 H), 2.04 (s, 12 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 140.5, 131.6, 129.7, 128.5, 126.5, 126.1, 124.2, 116.7, 37.3, 14.0, 12.3 ppm. $C_{42}H_{46}Cl_4Zr_2$ (875.07): calcd. C 57.65, H 5.30; found C 56.64, H 5.72.

Synthesis of [{[*p*-(3,4-$Me_2C_5H_2$)$C_6H_4CH_2$][$CpZrCl_2$]}$_2$] (2c): An identical procedure to that used for the synthesis of **2b** was employed with the ligand **1c** (0.366 g, 1.00 mmol) to afford **2c** as a light-yellow solid (0.573 g, 70%). ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.36 (d, 4 H), 7.12 (d, 4 H), 6.49 (s, 4 H), 6.11 (s, 10 H), 2.86 (s, 4 H), 2.15 (s, 12 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 140.8, 131.4, 129.4, 128.7, 125.1, 122.6, 116.5, 114.0, 37.3, 13.8 ppm. $C_{38}H_{38}Cl_4Zr_2$ (818.97): calcd. C 55.73, H 4.68; found C 55.74, H 4.87.

Synthesis of [*p*-(C_5Me_4)$C_6H_4CH_2$]$_2$[$TiCl_3$]$_2$ (3b): A slurry of **1b** (0.422 g, 1.00 mmol) in 20 mL of thf was treated with two equivalents of *n*BuLi (0.8 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 4 h to give a yellow suspension. Two equivalents of [ClTi(O*i*Pr)$_3$] (2.0 mmol, 0.521 g) dissolved in 10 mL of thf was added to the reaction mixture through a cannula at –78 °C. The resulting reaction mixture was then warmed to room temperature and stirred for 24 h. The golden-yellow solution formed was evaporated to dryness and extracted with 30 mL of CH_2Cl_2. The mixture was subsequently treated with an excess amount of Me_3SiCl (3 to 4 equiv.) at 0 °C. After warming to room temperature, the reaction mixture was further stirred overnight. During the course of the reaction, the slow formation of a red precipitate was observed. The resulting red mixture was evaporated, and the shiny red product was washed twice with 20 mL of a mixture of *n*-hexane and CH_2Cl_2 (4:1, v/v). Drying in vacuo afforded 0.445 g of scarlet microcrystals of **3b** in 61% yield. Recrystallization of a concentrated CH_2Cl_2 solution of **3b** layered with *n*-hexane at room temperature afforded red single crystals suitable for an X-ray diffraction study. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.24 (m, 8 H), 2.99 (s, 4 H), 2.46 (s, 12 H), 2.41 (s, 12 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 142.9, 142.0, 138.7, 136.1, 130.8, 130.3, 128.4, 37.3, 15.5, 14.6 ppm. $C_{32}H_{36}Cl_6Ti_2$ (729.08): calcd. C 52.72, H 4.98; found C 52.65, H 5.44.

Synthesis of [{[*p*-(3,4-$Me_2C_5H_2$)$C_6H_4CH_2$][$TiCl_3$]}$_2$] (3c): A similar procedure to that used for the synthesis of **3b** was employed with the ligand **1c** (0.366 g, 1.00 mmol), but with an excess of Me_2SiCl_2 instead of Me_3SiCl, to afford **3c** as a dark-red solid (0.451 g, 67%). ^1H NMR (400.13 MHz, CDC_{13}): δ = 7.57 (d, 4 H), 7.17 (s, 4 H), 7.10 (d, 4 H), 2.93 (s, 4 H), 2.47 (s, 12 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 143.3, 140.6, 139.3, 130.8, 129.2, 126.1, 119.1, 37.4, 16.0 ppm. $C_{28}H_{28}Cl_6Ti_2$ (672.97): calcd. C 49.97, H 4.19; found C 49.60, H 5.02.

Synthesis of [(1-*p*-tolyl-3,4-$Me_2C_5H_2$)$TiCl_3$] (5c): A similar procedure to that used for the synthesis of **3b** was employed with 1-tolyl-3,4-$Me_2C_5H_3$ (0.366 g, 1.00 mmol), but with an excess of Me_2SiCl_2 instead of Me_3SiCl, to afford **6c** as dark red microcrystals (0.432 g, 64% yield). ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.61 (d, 2 H), 7.22 (d, 2 H), 7.18 (s, 2 H), 2.47 (s, 6 H), 2.37 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 140.8, 140.4, 139.2, 130.2, 129.6, 126.0, 119.0, 21.4, 15.9 ppm. $C_{14}H_{15}Cl_3Ti$ (337.49): calcd. C 49.82, H 4.48; found C 49.42, H 4.61.

Ethylene Polymerization: Freshly distilled toluene (48 mL) was placed in a degassed 250-mL glass reactor charged with a pre-weighed amount of s-MAO (Al/Zr = 1000) and the temperature was adjusted using an external bath. The flask was then filled with ethylene monomer at 1 bar with vigorous stirring after degassing with the monomer several times. Polymerization was started by addition of a toluene solution of catalyst (2.0 mL, 2.0 µmol of Zr). After 2 min, all the reactions were quenched by addition of an acidified ethanol solution (10% HCl in EtOH) and the resulting polyethylene was precipitated by the addition of 200 mL of ethanol. After stirring for 1 to 2 h, the polyethylenes were filtered off, washed with ethanol several times, and dried under vacuum to a constant weight at 80 °C.

Styrene Polymerization: Freshly distilled toluene (48 mL) and styrene (5.0 mL) were successively added to a degassed, 250-mL glass reactor charged with a pre-weighed amount of s-MAO (Al/Ti = 1000) with vigorous stirring. The temperature was adjusted using an external bath. Polymerization was started by addition of a toluene solution of catalyst (2.0 mL, 10.0 µmol of Ti). After 20 min, all the reactions were quenched by addition of an acidified ethanol solution (10% HCl in EtOH) and the resulting polystyrene was further precipitated by addition of 200 mL of ethanol. After stirring for 1 to 2 h, polystyrenes were filtered off, washed with ethanol several times, and dried under vacuum to a constant weight at

80 °C. The crude polymer was extracted with refluxing 2-butanone for 12 h, and the insoluble fraction was filtered and dried under vacuum overnight at 80 °C in order to determine the syndiotactic polystyrene portion.

Polymer Analysis: The molecular weight (M_w) and molecular weight distribution (M_w/M_n) of polypropylenes were determined by GPC (Polymer Laboratories PL-GPC 220) in 1,2,4-trichlorobenzene using standard polystyrenes as a reference. The melting temperatures (T_m) of polypropylenes were measured by DSC (TA Instrument, 2910 MDSC).

X-ray Structure Determination: X-ray diffraction measurements were performed with a Bruker AXS diffractometer with a CCD area detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. A hemisphere of data was collected using ω scans. The frame data sets were processed using the SAINT and XPREP processing package. An empirical absorption correction was applied to each data set with the program SADABS. All the intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at their geometrically calculated positions and refined as riding on the corresponding carbon atoms with isotropic thermal parameters. For **2b**, final refinement based on the reflections with $I > 2\sigma(I)$ converged at $R1$ = 0.0348, $wR2$ = 0.0851, GOF = 0.963, and for **3b**, $R1$ = 0.0506, $wR2$ = 0.1156 and GOF = 0.845 (Table 4).[44]

Table 4. X-ray crystallographic data.

Compound	**2b**	**3b**
Formula	$C_{42}H_{46}Cl_4Zr_2$	$C_{32}H_{36}Cl_6Ti_2$
Formula weight	875.07	729.08
Crystal system; space group	monoclinic; *C*2/*c*	monoclinic; *C*2/*c*
a [Å]	21.509(5)	36.11(6)
b [Å]	16.944(4)	6.625(11)
c [Å]	12.933(3)	15.33(2)
α, β, γ [°]	90, 124.370(4), 90	90, 94.59(9), 90
V [Å^3]	3890.5(16)	3656(10)
Z	4	8
$D_{calcd.}$ [g cm^{-3}]	1.494	1.325
$F(000)$	1784	1496
T [K]	293	293
μ (Mo-K_α) [mm^{-1}]	0.839	0.895
θ range [°]	1.66–28.37	1.13–27.97
No. of unique/observed [$I > 2\sigma(I)$] reflections	4499/12111	4059/10577
No. of parameters refined	221	193
$R1$, $wR2$[a]	0.0348, 0.0851	0.0506, 0.1156
GOF	1.045	0.845
Min./max. electron density [e Å^{-3}]	–0.692/0.302	–0.360/0.313

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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