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Biphenylene-Bridged Dinuclear Group 4 Metal Complexes: Enhanced Polymerization Properties in Olefin Polymerization

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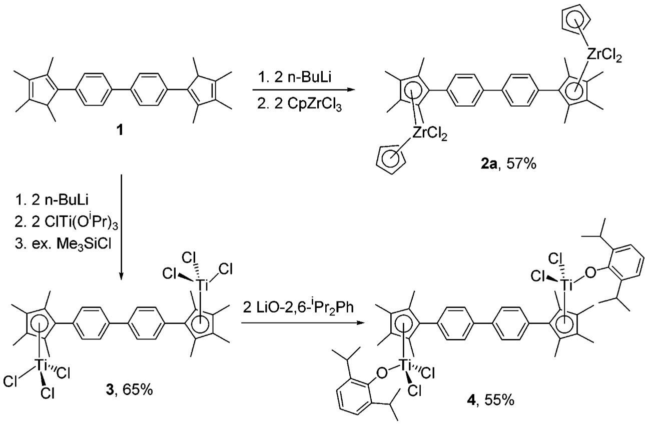
*Summary: The well-defined, novel dinuclear group 4 metal complexes [4,4′-(C_6H_4)$_2$(C_5Me_4)$_2$][CpZrX_2]$_2$ (X = Cl (**2a**), Me (**2b**)), [4,4′-(C_6H_4)$_2$(C_5Me_4)$_2$][TiCl_3]$_2$ (**3**), and [4,4′-(C_6H_4)$_2$(C_5Me_4)$_2$][Ti(O-2,6-^{i}Pr$_2$Ph)Cl$_2$]$_2$ (**4**) exhibit an increase of molecular weight as well as comparable or even higher catalytic activity in ethylene (**2** and **4**) and styrene (**3** and **4**) polymerization than their mononuclear counterparts.*

Dinuclear group 4 catalysts which consist of two linked active centers in a molecule have been recently investigated due to their potential catalytic properties in olefin polymerization, ascribed to cooperative effects between two active centers.[1] Although several studies on dinuclear catalysts connected by flexible bridging groups suggest that the polymerization properties such as catalyst activity and molecular weight of the polymer are strongly correlated with the nature of the bridging group employed,[2] systematic polymerization studies utilizing well-defined dinuclear catalyst systems have still been less explored in comparison with those of well-known mononuclear systems.[3] Herein, we report the synthesis and characterization of novel dinuclear group 4 complexes linked by a biphenylene-bridged bis(cyclopentadienyl) ligand, 4,4′-(C_6H_4)$_2$(C_5Me_4H)$_2$ (**1**), where the biphenylene group was chosen due to the nature of steric rigidity, a proper length, and electronic conjugation. Also, the direct comparison of their polymerization behavior in olefin polymerization with those of the corresponding mononuclear catalysts was described.

Transmetalation of the dilithium salt of the ligand **1**, prepared from the modified literature procedure,[4] with 2 equiv of CpZrCl_3 in refluxing THF afforded the dinuclear zirconocene complex [4,4′-(C_6H_4)$_2$(C_5Me_4)$_2$]-[CpZrCl_2]$_2$ (**2a**). The dinuclear half-titanocene complex [4,4′-(C_6H_4)$_2$(C_5Me_4)$_2$][TiCl_3]$_2$ (**3**) was synthesized from the reaction of the dilithium salt of **1** with 2 equiv of ClTi(O^{i}Pr)$_3$ in refluxing THF, followed by in situ chlorination with an excess amount of Me_3SiCl in CH_2Cl_2.[5] The complex **3** was further converted cleanly to the corresponding aryloxide complex [4,4′-(C_6H_4)$_2$(C_5Me_4)$_2$]-[Ti(O-2,6-^{i}Pr$_2$Ph)Cl$_2$]$_2$ (**4**) by treating it with 2 equiv of LiO-2,6-^{i}Pr$_2$Ph in THF (Scheme 1).

Scheme 1



The solid-state structures of **2a** and **4** have been determined by X-ray diffraction methods,[6] and the structure of **2a**[7] is depicted in Figure 1. The zirconium complex **2a** crystallizes in the space group $P2_1/n$ with only half of the molecule in the asymmetric unit. Thus, two [C_5Me_4Ph]CpZrCl_2 fragments are perfectly inverted with respect to the phenylene−phenylene single bond, indicating that **2a** consists of two equivalent units in the solid state. It can be also seen that the large biphenylene bridge is oriented away from the chlorine atoms. The detailed structural analysis indicates that the structural parameters around the zirconium center, such as the bond angles and bond distances listed in the caption to Figure 1, are in a range similar to those

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[6] See the Supporting Information for details.

[7] Crystal data for **2**: $C_{40}H_{42}Cl_4Zr_2$, M_r = 847.02, monoclinic, a = 9.312(2) Å, b = 15.201(3) Å, c = 13.422(2) Å, β = 101.35(0)°, V = 1862.8-(5) Å^3, T = 293 K, space group $P2_1/n$, Z = 4, μ(Mo Kα) = 0.874 mm^{-1}, 11 945 reflections measured, 4449 unique (R_{int} = 0.0203), which were used in all calculations. The final refinement based on 3581 reflections ($I > 2\sigma(I)$) converged at R1 = 0.0348 and wR2 = 0.0995.

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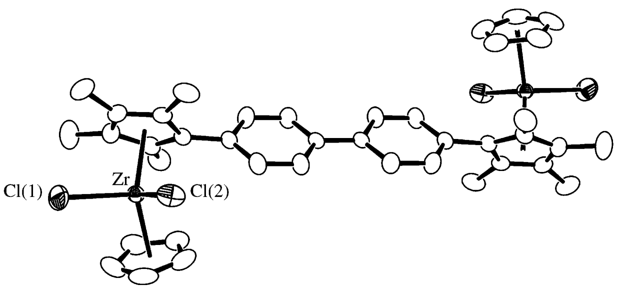
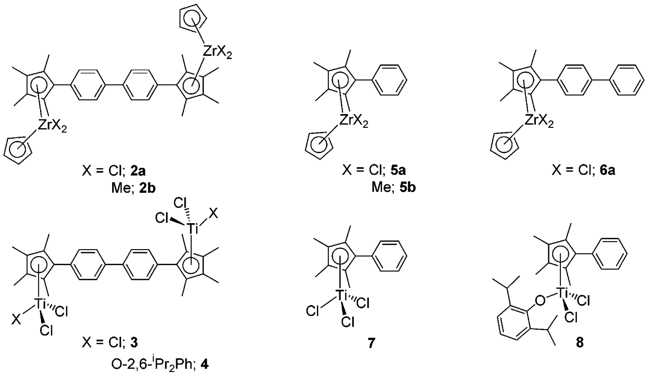


Figure 1. Molecular structure of [4,4′-$(C_6H_4)_2(C_5Me_4)_2$]-$[CpZrCl_2]_2$ (**2a**). Selected bond distances (Å) and angles (deg): Zr−Cl(1) = 2.429(1), Zr−Cl(2) = 2.440(1), Zr−Cg(1) = 2.224(1), Zr−Cg(2) = 2.199(2); Cl(1)−Zr−Cl(2) = 96.5(0), Cg(1)−Zr−Cg(2) = 129.8, Cp′(1)-Ph(1) = 63.6(2). Cg(1) and Cg(2) are the centroids of the C_5Me_4 and Cp rings, respectively, Cp′(1) is the plane of C_5Me_4, and Ph(1) is the plane of C_6H_4.

Chart 1



for mononuclear nonbridged zirconocene complexes.[8,9] Interestingly, the dihedral angle of 63.6(2)° between the C_5Me_4 ring and the adjacent phenylene ring is somewhat larger than that observed in the corresponding mononuclear zirconocene $(C_5Me_4Ph)CpZrCl_2$ (**5a**; 47.2°),[8] while the biphenylene group is nearly planar, showing no apparent distortion between two phenylene planes despite the possible presence of nonbonded repulsion interactions between the ortho hydrogen atoms. The structural analysis of the titanium complex **4**[6] also reveals that the overall features in **4** very much resemble those in **2a**, except for the fact that the Cp ring is replaced by the aryloxide group and the bonding geometry of each $[C_5Me_4Ph]Ti(OAr)Cl_2$ unit is nearly identical with that of similar mononuclear complexes.[10]

To investigate the catalytic properties of the dinuclear complexes in olefin polymerization, the ethylene polymerization behavior of the zirconocene complex **2a** was first examined along with those of the mononuclear catalysts **5a**[8] and $(C_5Me_4biPh)CpZrCl_2$ (**6a**)[6] (Chart 1).

In the presence of an excess amount of methylaluminoxane (MAO; Al/Zr = 1000 in Table 1), **2a** shows high activity, comparable to that of the sterically encumbered **6a** and slightly higher than that of **5a**, which is an exact half of **2a** (entries 1−3). Also, the polyethylene produced by **2a** exhibits a narrow molecular weight distribution (M_w/M_n) of 2.21, suggesting that the two zirconium centers in **2a** are identical and each of them behaves as a single-site catalyst, as expected from the crystal structure of **2a**. Importantly, the polyethylene from **2a** has a molecular weight that is much higher than those of the polyethylenes from **5a** and **6a**. Considering that the polyethylenes by the mononuclear catalysts **5a** and **6a** exhibit nearly similar values in molecular weight, the molecular weight increase caused by **2a** is remarkable.

Table 1. Ethylene Polymerization Data with Catalysts 2, 5, and 6a[a]

entry	cat. (amt, μmol)	cocat.	Al/Zr	yield (g)	A ($\times10^{-3}$)[b]	M_w ($\times10^{-3}$)	M_w/ M_n	T_m (°C)
1	**2a** (1.0)	MAO	1000	0.607	9.10	398	2.21	134.4
2	**5a** (2.0)	MAO	1000	0.551	8.26	299	2.14	137.0
3	**6a** (2.0)	MAO	1000	0.633	9.49	270	2.09	136.8
4	**2a** (1.0)	MAO	2000	0.789	11.83	294	2.11	135.9
5	**5a** (2.0)	MAO	2000	0.588	8.82	219	2.18	134.6
6	**2b** (1.0)	borate		0.445	6.67	779	2.13	135.1
7	**5b** (2.0)	borate		0.378	5.67	543	2.60	135.4

[a] Conditions: P(ethylene), 1 bar; T_p, 50 °C; solvent, 50 mL of toluene; t_p, 2.0 min; MAO, solid MAO; borate, $[Ph_3C][B(C_6F_5)_4]$; [B]/[Zr] = 1. [b] Activity is given in units of (kg of PE)/((mol of Zr) h bar).

Since the ion-pair structure of catalytically active species in the MAO-activated system could be much affected by the ligand environment and the amount of MAO employed,[11] which in turn may influence both the catalytic activity and the rate of termination reactions such as chain transfer to Al or β-H transfer reactions, further ethylene polymerizations in the presence of an increased amount of Al components and the absence of any of them were carried out to gain a brief insight into the polymerization behavior of the biphenylene-bridged dinuclear zirconocenes. The use of an increased amount of MAO (entries 4 and 5) or borate as a discrete activator (entries 6 and 7) did not change the catalytic trend that the dinuclear zirconocenes provide higher activity and molecular weight under otherwise identical conditions in comparison to their mononuclear analogues, implying that such a catalytic trend is intrinsic to the present dinuclear systems. The decreased molecular weight in both di- and mononuclear catalyst systems at the increased amount of MAO also indicates the involvement of chain transfer to Al under MAO activation, probably to a similar extent.[12] In addition, on activation with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$, the dimethyl complexes **2b** and **5b**[6] afforded polyethylenes with much increased molecular weight, reflecting prevailing chain transfer to Al under the above MAO-activated catalyst systems. Furthermore, the production of the higher molecular weight polymer by **2b** than by **5b** under borate activation suggests that ethylene polymerizations with the

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Table 2. Styrene and Ethylene Polymerization Data with Catalysts 3, 4, 7, and 8[a]

entry	cat. (amt, μmol)	monomer	yield (g)	A ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n	T_m (°C)	SI (%)[d]
1	**3** (5.0)	styrene[b]	0.590	0.177	51.8	1.79	272.2	95
2	**4** (5.0)	styrene[b]	0.552	0.166	57.0	1.86	272.3	95
3	**7** (10.0)	styrene[b]	0.361	0.108	37.2	1.70	272.5	90
4	**8** (10.0)	styrene[b]	0.525	0.157	56.5	1.76	272.2	93
5	**4** (2.5)	ethylene[c]	0.840	2.02	401	6.50	130.4	
6	**8** (5.0)	ethylene[c]	0.744	1.79	283	4.91	128.5	

[a] Conditions: solvent, 50 mL of toluene; [Al]/[Ti], 1000; T_p, 50 °C. [b] Conditions and definitions: [styrene], 5.0 mL; t_p, 20 min; MAO, modified MAO in toluene; activity given in units of (kg of PS)/((mol of Ti) h). [c] Conditions and definitions: P(ethylene), 1 bar; t_p, 5 min; MAO, solid MAO; activity given in units of (kg of PE)/((mol of Ti) h bar). [d] Syndiotacticity determined by 2-butanone-insoluble portion.

foregoing dinuclear zirconocenes are likely to proceed with reduced rates of β-H transfer reactions.

In the case of the dinuclear half-titanocenes **3** and **4**, their styrene polymerization behavior was compared with that of the corresponding mononuclear catalysts $(C_5Me_4Ph)TiCl_3$ (**7**)[13] and $(C_5Me_4Ph)Ti(O\text{-}2,6\text{-}{}^iPr_2Ph)Cl_2$ (**8**),[6,14] respectively. From the polymerization results in Table 2, it can be easily noted that **3** and **4** behave as highly active single-site catalysts for styrene polymerization. Moreover, **3** provides higher activity and molecular weight than its mononuclear counterpart **7** while **4** and **8** show similar styrene polymerization behavior. Further investigation of syndiotactic index (SI) and melting temperature (T_m) of the polystyrenes suggests that the syndiospecific stereocontrol is also well maintained in **3** and **4**.

According to the ethylene polymerization data with the dinuclear and mononuclear titanocene aryloxides **4** and **8** (entries 5 and 6 of Table 2), respectively, it is the dinuclear **4** that produces polyethylene with higher molecular weight at a slightly increased level of activity. Thus, the pattern of the increase in activity and molecular weight of the polymers that is consistently observed for **2**−**4** might be the characteristic polymerization property of the present dinuclear catalytic systems derived from the biphenylene-bridged bis(cyclopentadienyl) ligand **1**.

In conclusion, we have synthesized and characterized the well-defined dinuclear group 4 metallocene catalysts linked by a biphenylene bridge and examined their catalytic properties with the direct comparison with those for the corresponding mononuclear catalysts in the polymerization of ethylene and styrene. The dinuclear catalysts consistently exhibit an increase of molecular weight of polyethylene and polystyrene as well as high catalyst activity. The detailed polymerization behavior, including the origin of these interesting results and the synthesis of relevant dinuclear catalysts, is under investigation.

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Supporting Information Available: Text, tables, and figures describing the full synthesis, characterization, and polymerization procedure and detailed crystallographic data and ORTEP drawings for **2a** and **4**; crystallographic data for **2a** and **4** are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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