

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
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DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 378 FASE NACIONAL INCLUIDO CAPITULO I
TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II	FOLIOS: 36
ACT: 519 PRESENTACION	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
DILIA MARIA RODRIGUEZ D ALEMAN

Asunto: Radicación: 11-3211- -5
 Trámite: 11
 Evento: 378
 Actuación: 519
 Oficio: 17341
 Folios: 36

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/US2009/004047				
Fecha de Presentación Internacional	13/07/2009				

1. Documentos estudiados

Descripción:	Rad. N°11-003211-00000-0000	13/Enero/2011
Reivindicaciones:	Rad. N°11-003211-00000-0000	13/Enero/2011
Prioridad:	US 12/172,805	14/Julio/2008

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del capítulo primero del Título 10 de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada.

Para el caso de la presente solicitud, al verificar la tasa pagada, todo el ultimo capitulo reivindicatorio presentado se tendrá en cuenta para realizar el examen de patentabilidad.

Título de la solicitud: “Composiciones de catalizadores de metalloceno intermedio y sus productos poliméricos”.

El problema planteado en esta solicitud es la necesidad de proporcionar un sistema catalizador sin cromo que pueda producir un homopolímero o copolímero de poliolefina que tiene la combinación deseada de una distribución de peso molecular amplio y un bajo nivel de ramificación de cadena larga.

Para resolver este problema técnico la solicitud en estudio proporciona composiciones catalizadoras y procesos para polimerizar poliolefinas, debidamente definidos (Rad. N°11-003211-00000-0000, Págs. 2 – 4).

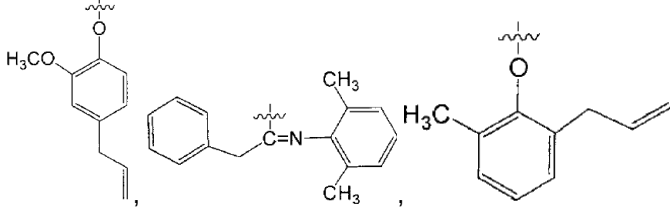
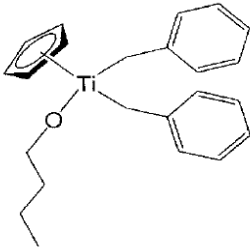
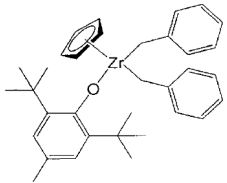
El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): B 01 J 31/22.

4. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

El capítulo reivindicatorio no se encuentran debidamente soportadas en la descripción puesto que en las realizaciones preferidas sólo hace referencia a los componentes de la composición catalizadora mencionados en la tabla 1, lo cual no evidencia que todas los posibles catalizadores mencionados se comporten de igual forma en la composición y en el proceso. Se sugiere restringir la solicitud a una razonable cantidad de catalizadores de acuerdo a lo probado, es decir, que se encuentran debidamente soportados en el capítulo descriptivo. Teniendo en cuenta la descripción en los ejemplos se encuentra:

Tabla 1. Ejemplos de los componentes de la composición catalizadora

Componente	Soporte de los ejemplos presentados	
Compuesto metalloceno híbrido	Metalocenos de formula (I) $\begin{array}{c} X^2 \\ \\ X^1 - M - X^3 \\ \\ X^4 \end{array}$	M: Zr
		X ¹ y X ² : bencilo
		X ³ : indenilo
		X ⁴ : 
	MET 1	
	MET 2	
Soporte activador	Sílice - alúmina fluorada (A-S1, sílice – alúmina y fluoruro ácido de amonio), alúmina sulfatada (A-S2, alúmina A y sulfato de amonio)	
Compuesto de órganoaluminio	triethylaluminio	

El solicitante debe definir específicamente la materia y el alcance de la invención a través de las características técnicas esenciales que se encuentren enteramente soportadas en la descripción.

La reivindicación 1 hace referencia a una composición pero no se mencionan los componentes y las proporciones de los mismos, por lo tanto se sugiere mencionar cuales son los componentes y sus proporciones. Puesto que hacen parte de las características esenciales de la invención.

En la reivindicación 1 la expresión “grupo alifático, aromático o cíclico sustituido o insustituido” es imprecisa puesto que abarca muchos compuestos, los cuales están definidos por su función dentro de la composición y no permite definir inequívocamente su estructura química, puesto que debe mencionar el número de carbonos de dichos grupos.

La reivindicación 11 menciona que la composición contiene un compuesto de organoaluminio que de ser parte importante de la composición debe mencionarse en la reivindicación 1, que es la independiente y contiene todas las características esenciales de la composición y según las realizaciones preferidas es parte de la composición. Por lo tanto mencionar dicho compuesto en su proporción en la composición de la reivindicación 1.

En la reivindicación 15 se menciona la expresión “bajo condiciones de polimerización”, pero no es claro cuáles son dichas condiciones, por lo tanto deben ser mencionadas puesto que hacen parte de las características esenciales que definen un proceso como lo son etapas y condiciones.

En las reivindicaciones 1 y 15 las expresiones “monómero de olefina”, “activador” y “cromonómero de olefina” son imprecisos puesto que esas expresiones abarcan muchos compuestos, los cuales están definidos por su función dentro de la composición y no permite definir inequívocamente su estructura química. Se sugiere modificar estas expresiones por el nombre común o IUPAC de los componentes preferidos.

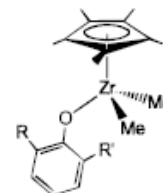
5. Determinación del Estado de la Técnica

El Estado de la Técnica se determinó con base en la Fecha de Presentación de la Solicitud de Prioridad, Julio 14 de 2008 y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

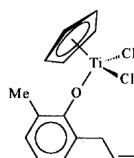
Ítem	Documento	Título	Fecha de publicación*
D1	Arevalo S., et Al, Journal of Organometallic Chemistry, 690, Págs. 4620 – 4627	“Ethylene polymerization behavior of monometallic complexes and metallodendrimers based on cyclopentadienyl-aryloxy titanium units”	2005
D2	Antiñolo A. et Al, Organometallics, ACS, vol. 19, No 15, Págs. 2837 – 2843	“Synthesis of Zirconium(IV) Monocyclopentadienyl-Aryloxy Complexes and Their Use in Catalytic Ethylene Polymerization. X-ray Structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}\{2,6\text{-OC}_6\text{H}_3(\text{CH}_3)_2\}_3$ ”	24/Julio/2000
D3	Thorm M., et Al, Organometallics, ACS, vol. 19, No 26, Págs. 5636 – 5642	“Synthesis, Characterization, and One-Electron Reduction of Mixed-Cyclopentadienyl/Aryloxy Titanium Dichlorides”	25/Diciembre/2000
D4	Arevalo S., et Al, Organometallics, 22, Págs. 5109 – 5113	“Synthesis of Aryloxy Cyclopentadienyl Group 4 Metal-Containing Dendrimers”	2003
D5	US2005113243	“Catalyst compositions for producing polyolefins in the absence of	26/Mayo/2005

		cocatalysts"	
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El documento D1 ^[1] divulga un sistema catalizador que comprende un compuesto 9 y un activador MAO (metilaluminoxano), el compuesto 9 presenta una baja actividad catalizadora en la polimerización de etileno tras una activación con exceso de MAO. Además se menciona el proceso de polimerización de etileno, con las condiciones de tiempo y los reactivos (Pág. 4623, esquema 1; Pág. 4624; Pág. 4626, numeral 4.8)

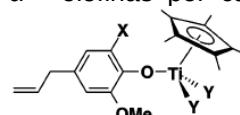


El documento D2 ^[2] divulga una combinación catalizador que comprende compuesto 6 , junto con un activador MAO, para la polimerización de etileno. Se menciona un proceso con proporciones de los reactivos, temperatura y tiempo (Pág. 2838, columna izquierda y esquema 2; Págs. 2840 – 2841)



El documento D3 ^[3] divulga un compuesto 18 sólido naranja, donde se menciona su proceso de obtención y es caracterizado por difracción de rayos X (Pág. 5637, Esquema 2)

El documento D4 ^[4] divulga compuestos catalizadores, empleados en la polimerización Ziegler – Natta de α - olefinas por catálisis homogénea. Donde los catalizadores son los compuestos los compuestos



X = H; Y = Cl (1), Me (8)
X = OMe; Y = Cl (2), Me (9) (Pág. 5109, Introducción; Pág. 5111, Esquema 3)

El documento D5 ^[5] divulga una composición catalizadora compuesta por a) un metalloceno; b) un óxido sólido tratado químicamente que comprende un óxido sólido tratado con anión de extracción de electrones, donde el óxido sólido es seleccionado de sílice, alúmina, fosfato de aluminio, entre otros y el anión de extracción de electrones es seleccionado de fluoruro, cloruro, entre otros (Pág. 1, Párrs. [0005] y [0006]; Pág. 1, Párr. [0017] a Pág. 2, Párr. [0019]; Pág. 2, Párrs. [0028] – [0037]; Pág. 7, Párrs. [0110] y [0112]).

6. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La **reivindicación 1** consiste en una composición catalizadora que comprende unos componentes debidamente definidos (Rad. N°11-003211-00000-0000, Pág. 74).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2
Composición catalizadora que comprende:	Sistema catalizador que comprende:	Combinación catalizador que comprende:

¹ anexo 1. D1

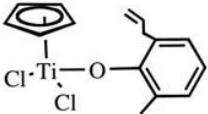
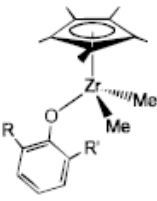
² anexo 2. D2

³ anexo 3. D3

⁴ anexo 4. D4

⁵ URL: [http://worldwide.espacenet.com/publicationDetails/biblio?](http://worldwide.espacenet.com/publicationDetails/biblio?DB=worldwide.espacenet.com&II=1&ND=3&adjacent=true&locale=en_EP&FT=D&date=20050526&CC=US&NR=2005113243A1&KC=A1)

[DB=worldwide.espacenet.com&II=1&ND=3&adjacent=true&locale=en_EP&FT=D&date=20050526&CC=US&NR=2005113243A1&KC=A1](http://worldwide.espacenet.com&II=1&ND=3&adjacent=true&locale=en_EP&FT=D&date=20050526&CC=US&NR=2005113243A1&KC=A1)

Un compuesto de metalloceno híbrido de fórmula (I) $\begin{array}{c} X^2 \\ \\ X^1 - M - X^3 \\ \\ X^4 \end{array}$		
M: Zr, Hf o Ti		
X ¹ y X ² : haluro o un grupo alifático, aromático o cíclico sustituido o insustituido	 compuesto 9 (Pág. 4623, esquema 1)	 Compuesto 6 donde R es C ₃ H ₅ Y R' es Me (Pág. 2838, esquema 2)
X ³ : grupo ciclopentadienilo, indenilo o fluorenilo sustituido o insustituido		
X ⁴ : -O-R ^A , -NH-R ^A , -PH-R ^A , -S-R ^A o -CR ^B =NR ^C , donde R ^A es un grupo arilo sustituido con un alquenilo, entre otros; R ^B y R ^C : H o grupo alifático, entre otros		
Un activador	Un activador MAO (Pág. 4623, Col. izquierda)	Un activador MAO (Pág. 2838, Col. izquierda)

Es posible concluir que las características **esenciales** de la composición de la reivindicación 1, habían sido divulgadas previamente en D1 y D2 porque de acuerdo con la tabla anterior donde se comparan las características técnicas de la reivindicación de manera independiente con las anterioridades D1 y D2 se concluye que la composición de la reivindicación 1, ya era conocido en el estado de la técnica como se evidencia con las anterioridades encontradas.

En consecuencia, la reivindicación 1 carece de novedad, según lo divulgado de manera independiente en cualquiera de los documentos D1 y D2.

Las reivindicaciones dependientes 2 – 6 no mencionan alguna característica que haga nuevo a la composición de la reivindicación 1, por lo cual se considera que no son nuevas.

La **reivindicación 15** consiste en un proceso de polimerización de olefina debidamente definido (Rad. N°11-003211-00000-0000, Pág. 77).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1
Proceso de polimerización que comprende:	Proceso de polimerización que comprende:
Poner en contacto la composición catalizadora con un monómero de olefina	Agregar el sistema catalizador al etileno (Pág. 4624, último párrafo antes del numeral 3; Pág. 4626, Numeral 4.8)

Es posible concluir que las características **esenciales** del proceso de la reivindicación 15, habían sido divulgadas previamente en D1 porque de acuerdo con la tabla anterior donde se comparan las características técnicas de la reivindicación con la anterioridad D1 se concluye que el proceso de la reivindicación 15, ya era conocido en el estado de la técnica como se evidencia con la anterioridad encontrada.

En consecuencia, la reivindicación 15 carece de novedad, según lo divulgado en el documento D1.

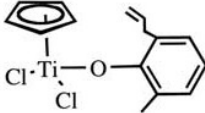
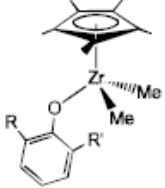
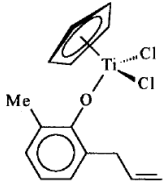
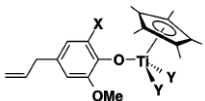
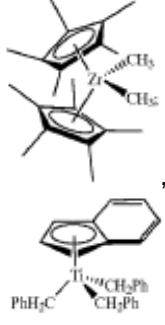
Las reivindicaciones dependientes 16 y 17 no mencionan alguna característica que

haga nuevo al proceso de la reivindicación 15, por lo cual se considera que no son nuevas.

Nivel Inventivo (Art18 D486)

La **reivindicación 8** consiste en una composición catalizadora que comprende unos componentes debidamente definidos (Rad. N°11-003211-00000-0000, Pág. 75).

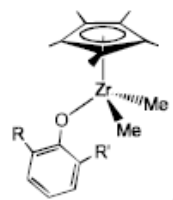
Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2	D3	D4	D5
Composición catalizadora que comprende:	Sistema catalizador que comprende:	Combinación catalizador que comprende:	Catalizador que comprende:	Compuestos	Composición catalizadora que comprende:
Un compuesto de metalloceno híbrido de fórmula (I) $\begin{array}{c} X^2 \\ \\ X^1-M-X^3 \\ \\ X^4 \end{array}$ M: Zr, Hf o Ti X¹ y X²: haluro o un grupo alifático, aromático o cíclico sustituido o insustituido X³: grupo ciclopentadienilo, indenilo o fluorenilo sustituido o insustituido X⁴: -O-R^A, -NH-R^A, -PH-R^A, -S-R^A o –CR^B=NR^C, donde R^A es un grupo arilo sustituido con un alquenilo, entre otros; R^B y R^C: H o grupo alifático, entre otros	 compuesto 9	Compuesto 6  donde R es C₃H₅ Y R' es Me	Compuesto 18 	 Compuesto 1 si X=H; Y=Cl Compuesto 2 si X=OMe; Y=Cl Compuesto 8 si X=H; Y=Me Compuesto 9 si X=OMe; Y=Me	Un metalloceno, tal como 
Un activador que es un soporte activador que comprende un óxido sólido que puede ser	Un activador MAO	Un activador MAO			Un óxido sólido que puede ser sílice, alúmina, entre otros, tratado con anión de extracción de

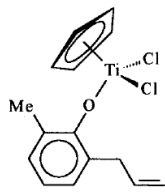
sílice, alúmina, entre otros, tratado con anión de extracción de electrones, tal como fluoruro, cloruro, entre otros					electrones, tal como fluoruro, cloruro, entre otros
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Los documentos D1 a D4 son considerados el estado de la técnica cercano a la invención definida en la reivindicación 8 porque:

D1 divulga un sistema catalizador que comprende un compuesto 9 y un activador MAO (metilaluminoxano), el compuesto 9 presenta una baja actividad catalizadora en la polimerización de etileno tras una activación con exceso de MAO. Además se menciona el proceso de polimerización de etileno, con las condiciones de tiempo y los reactivos (Pág. 4623, esquema 1; Pág. 4624; Pág. 4626, numeral 4.8)

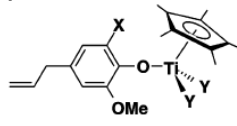


D2 divulga una combinación catalizador que comprende compuesto 6 , donde R es C3H5 Y R' es Me (Pág. 2838, esquema 2) junto con un activador MAO (Pág. 2838, Col. izquierda) para la polimerización de etileno. Se menciona un proceso con proporciones de los reactivos, temperatura y tiempo (Págs. 2840 – 2841)



D3 divulga un compuesto 18 solido naranja, donde se menciona su proceso de obtención y es caracterizado por difracción de rayos X (Pág. 5637, Esquema 2)

D4 divulga compuestos catalizadores, empleados en la polimerización Ziegler – Natta de α - olefinas por catálisis homogénea. Donde los catalizadores son los compuestos



los compuestos $\begin{matrix} X = H; & Y = Cl (1), Me (8) \\ X = OMe; & Y = Cl (2), Me (9) \end{matrix}$ (Pág. 5109, Introducción; Pág. 5111, Esquema 3)

La diferencia entre la invención, definida en la reivindicación 8 y el sistema catalizador del documento D1 consiste en que no se menciona que el activador sea un soporte activador.

La diferencia entre la invención, definida en la reivindicación 8 y la combinación catalizador del documento D2 consiste en que no se menciona que el activador sea un soporte activador.

La diferencia entre la invención, definida en la reivindicación 8 y el catalizador del documento D3 consiste en que no se menciona la presencia de un activador.

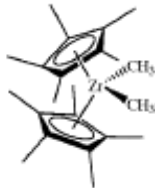
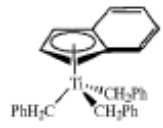
La diferencia entre la invención, definida en la reivindicación 8 y el catalizador del documento D4 consiste en que no se menciona la presencia de un activador.

El efecto que lograría la diferencia del tipo de activador en la composición catalizadora antes mencionada en la reivindicación 8, no puede ser determinado toda vez que no existe alguna evidencia que indique que dicha diferencia, otorgan a la composición ahora reivindicada una ventaja técnica sobre lo descrito en D1 o D2 o D3 o D4.

Por lo tanto, el problema técnico objetivo a resolver consiste en plantear una alternativa a la composición catalizadora conocida según D1 o D2 o D3 o D4 para ser empleada en el proceso de polimerización.

Sin embargo es conocido composiciones catalizadores para la polimerización de etileno que contiene oxido sólido, lo cual es divulgado en D5 que menciona una composición catalizadora compuesta por a) un metalloceno; b) un oxido solido tratado químicamente que comprende un oxido solido tratado con anión de extracción de electrones, donde el óxido solido es seleccionado de sílice, alúmina, fosfato de aluminio, entre otros y el anión de extracción de electrones es seleccionado de fluoruro, cloruro, entre otros (Pág. 1, Párrs. [0005] y [0006]; Pág. 1, Párr. [0017] a Pág. 2, Párr. [0019]). Además la composición comprende un co-catalizador organoaluminio, seleccionado de la formula $Al(X^5)_n(X^6)_{3-n}$, también puede ser un organozinc o un aluminoxano (Pág. 2, Párrs. [0028] – [0037]). Donde el compuesto de metalloceno

puede ser titanio (IV) trisbencil(indenil)



bis(pentametilciclopentadienil)zirconio dimetil (Pág. 7, Párrs. [0110] y [0112]).

Teniendo en cuenta lo expuesto anteriormente, la personas de nivel medio versada en la materia derivara de manera obvia la composición descrita en la reivindicación 8 de la presente invención a partir de las enseñanzas de la composición del documento D1 o D2 o D3 o D4 y de incluir el hecho que ya es conocido emplear un oxido sólido y un activador en la polimerización de olefina de D5, por lo tanto las diferencias se limitan en seleccionar un tipo de activador, sin que ese hecho confiera la polimerización de una olefina que tiene la combinación deseada de una distribución de peso molecular amplio y un bajo nivel de ramificación de cadena larga. Por lo tanto al combinar D1 con D5 o D2 con D5 o D3 con D5 o D4 con D5 la reivindicación resulta obvia. Puesto que las reivindicaciones dependientes 9 – 14 no mencionan características inventivas adicionales, tampoco puede ser considerada inventiva.

Conclusión:

Las reivindicaciones 8 – 14 cumplen el requisito de novedad (Art. 16), pero no cumplen con el requisito de nivel inventivo (Art. 18).

7. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	Arevalo S., et Al, Journal of Organometallic Chemistry, 690, Págs. 4620 – 4627	1 – 6 y 15 – 17 / 8 – 14	Novedad/Nivel inventivo
D2	Antiñolo A. et Al, Organometallics, ACS, vol. 19, No 15, Págs. 2837 – 28 43	1 – 6 / 8 – 14	Novedad/Nivel inventivo
D3	Thorm M., et Al, Organometallics, ACS, vol. 19, No 26, Págs. 5636 – 5642	8 – 14	Nivel inventivo
D4	Arevalo S., et Al, Organometallics, 22, Págs. 5109 – 5113	8 – 14	Nivel inventivo
D5	US2005113243	8 – 14	Nivel inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir del día siguiente de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2013-09-17

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Ethylene polymerization behavior of monometallic complexes and metallodendrimers based on cyclopentadienyl-aryloxy titanium units

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Abstract

Titanium-containing carbosilane dendrimers of type $n\text{G-Si}[(\text{CH}_2)_3\{\text{C}_6\text{H}_4-y(\text{OMe})_y\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_x$, in which phenoxy group is anchored to the dendritic skeleton in *para* position through eugenol or 2-allyl-2,6-dimethoxyphenol precursors, were used in ethylene polymerization. Fresh toluene solutions of these dendrimers in conjunction with MAO behaved as moderate active systems. However, their aged toluene solutions, when they were activated with MAO became highly active catalysts as result of dendrimer aggregation processes. However, when the peripheral unit are replaced by $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2]$ or $[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}]$ groups or 2-allyl-6-methylphenol are incorporated to the peryphery of a carbosilane dendrimer no aggregation was observed upon aging.

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Keywords: Aryloxy; Dendrimer; Titanium; Ethylene; Aggregation

1. Introduction

The interest of dendrimers functionalized with metals at the periphery as catalysts, arises mainly from their ability to combine the advantages of homogeneous and heterogeneous catalysis in one system [1]. Moreover, their shape and size make them more suitable for recycling than soluble polymer-supported catalysts. The multiple reaction sites located at their surfaces may afford reaction rates comparable to those shown in homogeneous systems due to the accessibility for the substrate. However, catalytic efficiency of dendrimers concerning olefin polymerization is often lower than that of their monomeric counterparts, due to factors as, for instance, the congestion of the surface or the improvement of bimetallic deactivation mechanisms. In this context, Seyferth synthesized carbosilane dendrimers with eight

peripheral zirconocene groups that showed considerable activity in the polymerization of ethylene [2], although they were ten times less active than monomeric zirconocenes. In contrast, for some other homogeneous processes, higher activities respecting to the mononuclear counterparts have been observed [3]. Recently we have published the synthesis of aryloxo cyclopentadienyl titanium-containing carbosilane dendrimers [4,5] of type $n\text{G-Si}[(\text{CH}_2)_3\{\text{C}_6\text{H}_4-y(\text{OMe})_y\}\text{O}]\text{Ti}(\text{C}_5\text{R}_5)\text{Cl}_2]_x$ (see an example in Fig. 1) using as precursor 4-allyl-2-methoxyphenol (commonly called eugenol) or 4-allyl-2,6-dimethoxyphenol, although no catalytic applications were described.

In this paper, we report on the use of these systems in the polymerization of ethylene and the different behavior observed depending on the aging of the precatalyst solution. As a comparison, the synthesis and catalytic behavior of new and analogous aryloxo cyclopentadienyl group 4 complexes based on the more encumbered precursor 2-allyl-6-methylphenol are also presented.

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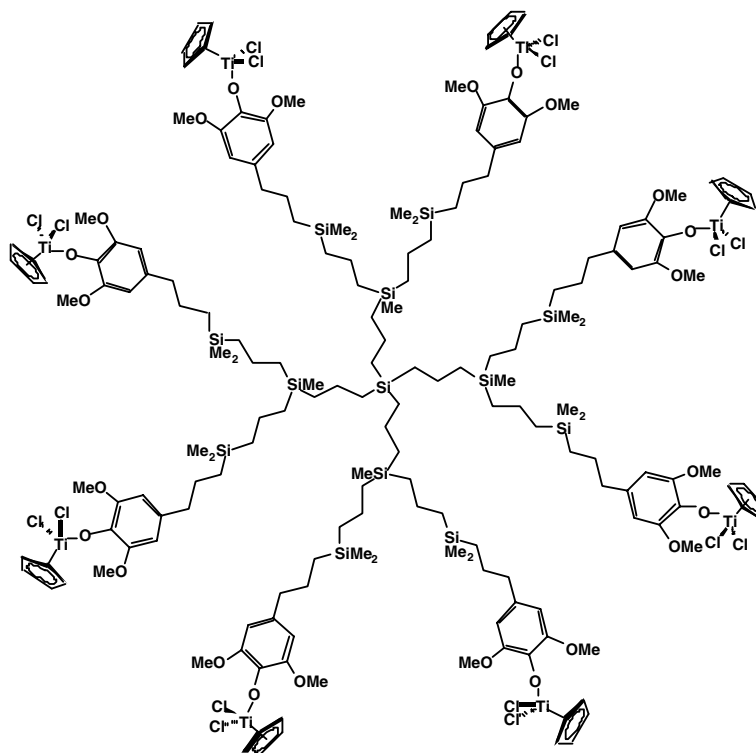


Fig. 1. Molecular representation of the second generation organotitanium-containing dendrimer $\text{Si}[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_3\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_8$ (**4**).

2. Results and discussion

Fresh toluene solutions of the dendrimers $n\text{G-Si}[(\text{CH}_2)_3\{\text{C}_6\text{H}_{4-y}(\text{OMe})_y\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_x$ ($n=1$, $x=4$, $y=1$ (**1**), $y=2$ (**2**); $n=2$, $x=8$, $y=1$ (**3**), $y=2$ (**4**); $n=4$, $x=32$, $y=1$ (**5**), $y=2$ (**6**)) [4] and the monometallic derivatives $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_{4-y}(\text{OMe})_y(\text{C}_3\text{H}_5)\}\text{Cl}_2]$ ($y=1$ (**7**); $y=2$ (**8**)) [4] in which the aliphatic aryloxy substituent is in *para* position to the O function, polymerized ethylene upon activation with methylaluminoxane (MAO) at 1 bar of ethylene pressure with moderate efficiency, according to Gibson classification [6]. Metallo-dendrimers of first generation performed activities ($101 \text{ gPE mmol}^{-1} \text{ h}^{-1}$ (**1**) and $134 \text{ gPE mmol}^{-1} \text{ h}^{-1}$ (**2**)) comparable to that shown by monometallic complexes **7** ($144 \text{ gPE mmol}^{-1} \text{ h}^{-1}$) and **8** ($154 \text{ gPE mmol}^{-1} \text{ h}^{-1}$), $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ ($173 \text{ gPE mmol}^{-1} \text{ h}^{-1}$), $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2\{\text{O}-2,6\text{-iPr}_2(\text{C}_6\text{H}_3)\}]$ [7], or silsesquioxane derivatives [8]. However, the catalytic activities dropped down to $29\text{--}34 \text{ gPE mmol}^{-1} \text{ h}^{-1}$ for second and fourth generation dendrimers, probably for the same reasons mentioned above. Nevertheless, when toluene solutions of dendritic precatalysts **1–6** were aged alone, prior to be added to a toluene solution containing MAO as cocatalyst, significant changes in the activities were detected. In three weeks, the first generation dendrimers doubled their activities while a dramatic increase, more than 40 times, was observed for second and fourth generation ($525\text{--}800 \text{ gPE mmol}^{-1} \text{ h}^{-1}$). During the aging of the

precatalyst solutions, it was observed the slow precipitation of red oils which could not be redissolved by heating or with polar solvents for their spectroscopic characterization by NMR and reduces the concentration of titanium center in the solution. The positive behavior in terms of activity, cannot be ascribed either to changes in the Al/Ti ratio, because polymerization experiments carried out at different molar proportions do not produce significant increases, or to heterogeneous processes caused by the insoluble precipitate which do not polymerize ethylene. Another explanation may be the existence of different species arising from the transformation of the metallodendrimers during the aging process, for instance the presence of titanocene as a result of a ligand exchange, or μ -oxo titanium species along with dendrimers including phenol ended branches due to partial hydrolysis. For the later example, some authors have published the enhancement of the productivity and molecular weight by modification of MAO with phenols [9]. However, chemical transformation of the aged precatalysts can be ruled out because the ^1H NMR spectra of the soluble part of the precatalysts remain unchanged over the course of the aging process. Besides, the molecular weights of the polymers are more than ten times higher than those obtained with the titanocene derivative [10]. The changes in activity and molecular weights seem to be too high for an undetectable or partial hydrolysis suffered for these dendrimers.

In a systematic study, a toluene solution of dendrimer **4** was aged before activation with MAO, to accomplish ethylene polymerization at different aging times (see Table 1 and Section 4 for procedure). The activity reached a maximum at 5 weeks (entry 5, activity 1365 gPE mmol⁻¹ h⁻¹). At this point, the dendrimer became a highly active catalyst [6]. From this time onwards, the activity decay was probably due to the presence of very low titanium concentrations resulting from the precipitation of the red oils above mentioned. The molecular weights ($M_w = 663,000$ – $1,000,400$) and polydispersities ($M_w/M_n = 1.5$ – 1.6), measured at the same aging times, are shown in Table 1. The values obtained are of the same order or even higher than those found for the monometallic complex **8** ($M_w = 826,000$, $M_w/M_n = 1.5$). Hence, these values suggest that the aging process is not responsible of the high molecular weights and low polydispersities. Instead of that, the environment around the metal centers may be responsible of such effects. Indeed, the presence of alkyl substituents in *ortho* position of the aryloxy ligand like in Nomura complex [Ti(C₅H₅)Cl₂{O-2,6-*i*Pr₂(C₆H₃)}] [7], afforded polyethylene of lower molecular weight and higher polydispersity ($M_w = 597,300$, $M_w/M_n = 3.3$) under 4 atm of ethylene pressure and 60 °C. Other authors have published lower values of $M_w = 336,866$, $M_w/M_n = 2.65$ using the same precatalyst at 1 atm and room temperature [11]. It is possible to assume that the presence of *ortho* OMe groups in the aryloxy fragment allows an additional electronic stabilization of the active species increasing the propagation rate. Respecting the polydispersities, these are consistent with a single-site catalyst, ruling out the possibility of other type of polymerization being the responsible of the behavior observed after the aging time. In Table 1 are also recorded the melting points and enthalpies as well as the crystallinity percentage measured by differential scanning calorimetry (DSC). Both, monometallic complex **8** and the different entries of **4** afforded melting point values in a range of 135–137 °C consistent with high density polyethylene (HDPE) [12]. The most noticeable feature was the higher crystallinity percentage (57%) induced by the

dendrimer **4**, even with a freshly prepared catalyst, compared to monometallic derivative **8** (39%) and hence independent of the aging processes but reliant on the dendritic nature.

Dynamic light-scattering experiments on a 6 mM toluene solution of dendrimer **4** at different aging times showed the presence of time-dependent aggregates (see Fig. 2) [13]. The average hydrodynamic diameters were too small to be determined with accuracy at the initial

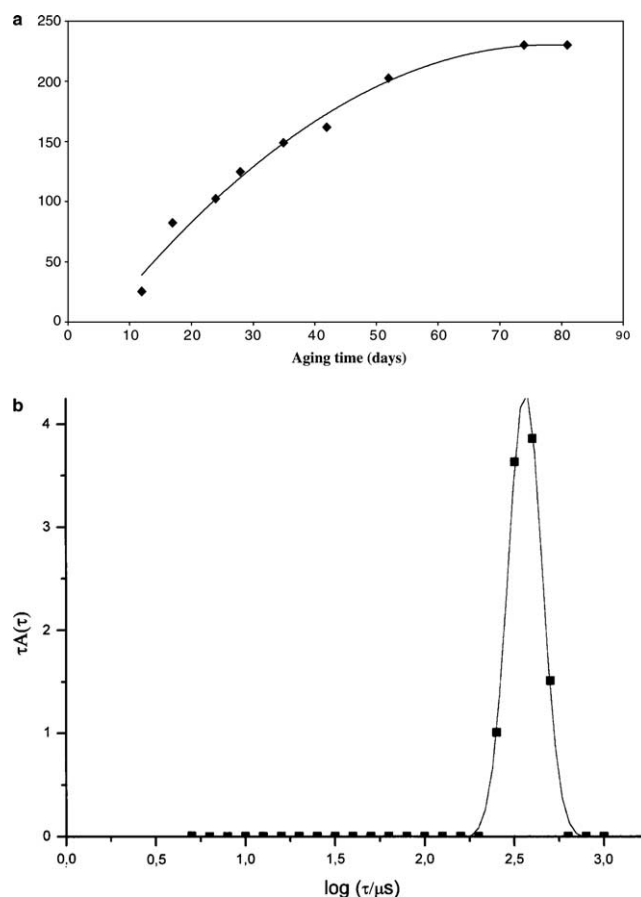


Fig. 2. (a) Plot of hydrodynamic diameter of dendrimer **4** aggregates versus aging time. (b) Distribution function of relaxation time for the dendrimer **4** with 28 days of aging time.

Table 1

Ethylene polymerization with dendrimer **4** and the monometallic derivative **8** using aged precatalyst solutions^a

Entry	Precatalyst	Aging time (weeks)	Yield (mg)	Activity (gPE mmol ⁻¹ h ⁻¹)	M_w	M_w/M_n	T_m (°C)	ΔH (J g ⁻¹)	Crystallinity α (%)
1	4	0	7.0	34			136	–155	54
2	4	1	90.7	435	663,000	1.51	135	–164	57
3	4	3	173.2	831	732,300	1.61	137	–169	59
4	4	5	284.3	1365	1,004,000	1.56	135	–170	59
5	4	6	219.3	1053	784,600	1.51	135	–165	57
6	4	7	148.3	712			136	–165	57
7	8 ^b	0	32.0	154	826,000	1.50	136	–113	39

^a Conditions: Al/Ti: 1000/1, [Ti] = 25 μ M, 50 mL of toluene, $t = 10$ min, $T = 20$ °C, $p = 1$ atm, MAO as cocatalyst.

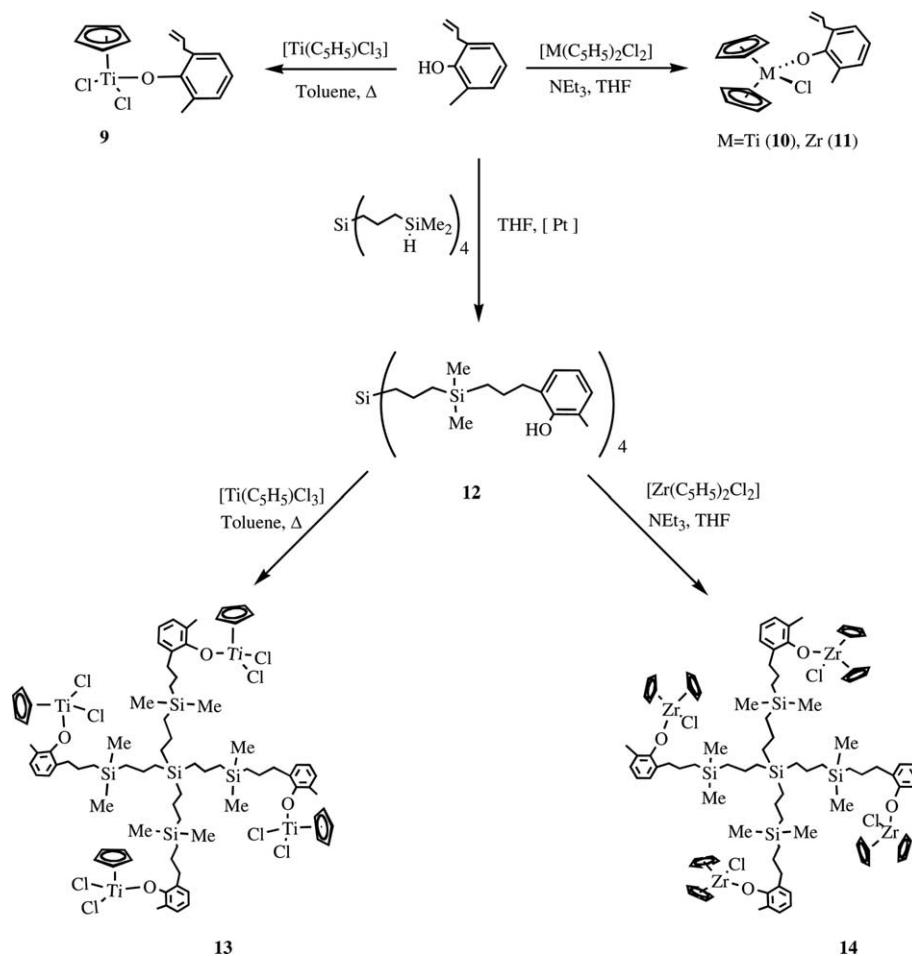
^b No significant changes observed when precatalyst is aged.

stages in which dendrimer **4** should be mainly unaggregated. The aggregate growth reached a plateau at ca. 74 days with hydrodynamic diameters of 229 nm. In addition, the polydispersity of the particle sizes was low as determined by the quality factor (less than 0.07). This feature was confirmed by the function of the relaxation time distribution from which only one dynamic process with a narrow distribution was observed (see Fig. 2). This result evidences the physical nature of the aggregation process and rules out the hydrolysis reaction mentioned above or other type of chemical aggregations.

Interestingly, when $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]$ was replaced by $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2]$ or $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}]$ as peripheral units [5], and the toluene solutions were aged before activation with MAO, no aggregation and no changes in the catalytic activities, were observed. The activities found for all these systems are comparable to those obtained with the well established compounds $[\text{Ti}(\text{C}_5\text{Me}_5)_3\text{Cl}_3]$ or $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$.

In an attempt to shed light on the behavior above described, we prepared new aryloxo-cyclopentadienyl group 4 complexes based on the ligand precursor 2-allyl-6-methylphenol (Scheme 1). In these complexes

the aliphatic aryloxy substituent is in *ortho* position to the O function, which means altered electronic and steric properties. The reaction of 2-allyl-6-methylphenol with one equivalent of $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ in toluene or one equivalent of $[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) in tetrahydrofuran and in the presence of triethylamine, leads to the monometallic aryloxo mono- and bis-cyclopentadienyl complexes $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_3(\text{Me})(\text{C}_3\text{H}_5)\}\text{Cl}_2]$ (**9**) and $[\text{M}(\text{C}_5\text{H}_5)_2\{\text{OC}_6\text{H}_3(\text{Me})(\text{C}_3\text{H}_5)\}\text{Cl}]$ ($\text{M} = \text{Ti}$ (**10**); Zr (**11**)) in high yields. **Complex 9** has been previously reported elsewhere [14] using a different synthetic approach with lower yields. Hydrosilylation of the allyl group of the phenol with the carbosilane system $[\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H})_4]$ [15] using the Karstedt catalyst [16], affords the polyphenol ligand 1G-Si $[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{Me})\}\text{OH}]_4$ (**12**). Reaction of **12** with four equivalents of $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ gives the polymetallic complex 1G-Si $[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{Me})\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2)_4$ (**13**) as an oily red solid in very good yield. Analogously, **12** reacts with four equivalents of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ to give the zirconium derivative 1G-Si $[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{Me})\}\text{O}]\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}]_4$ (**14**). However, a similar reaction with $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ does not lead to a polymetallic



Scheme 1.

complex of titanium analogous to **6**. This behavior must be attributed to steric hindrance caused by the proximity of the phenol functionality to the carbosilylated chain. The same argument is valid to explain why it is not possible to prepare the second generation dendrimer of **13** similar to those that we obtained when, for instance, eugenol is used instead of 2-allyl-6-methylphenol [4,5].

The steric requirement of the 2-allyl-6-methylphenoxy group causes also the fluxional behavior observed in solution for complex **10** due to the spin restriction around the O–Ph bond. The ^1H NMR resonances assigned to the methyl and allyl substituents of the phenol group appear clearly broadened when the spectrum of the titanocene **10** is registered in a 300 MHz spectrometer at room temperature in chloroform- d_1 . The dynamical origin of this broadening was confirmed lowering the temperature to $-50\text{ }^\circ\text{C}$, at which point methyl and allyl resonances are split in two sets of well-defined resonances with a ca. 2/1 integral ratio (see Section 4). This dynamical behavior is explained by the steric restrictions imposed by the *ortho* substituents on the O–Ph bond rotation, which allows the observation of two rotamers, one with the methyl and another with the allyl group in the *endo* position of the titanocene molecule. The activation barrier for the O–Ph bond rotation is estimated in $52 \pm 2\text{ kJ mol}^{-1}$ in CD_2Cl_2 . On other hand, only a set of well-defined resonances was observed for zirconocene **11** even at $-80\text{ }^\circ\text{C}$ ($\Delta G^\ddagger < 30\text{ kJ mol}^{-1}$), in agreement with the steric nature of the rotational restrictions.

$\{^1\text{H}-^{29}\text{Si}\}$ -HMBC experiments were used to locate silicon atom resonances for **12–14**, which are centered at 1.44 ppm (inner Si) and at 1.55 ppm (outer Si). IR spectra of complexes **10** and **13** show a band at ca. 560 cm^{-1} corresponding to $\nu(\text{Ti}-\text{O})$ and three signals at ca. 1210, 1020 and 910 cm^{-1} due to the presence of the $\text{C}_{\text{Ph}}-\text{O}$ bond.

Compounds **9–14** are soluble in chlorinated and aromatic solvents and insoluble in saturated hydrocarbons. The organometallic compounds are thermally stable but moisture sensitive. Spectroscopic and analytical data of all complexes are collected in Section 4 and are consistent with the proposed formulation.

Complexes **9** and **13** showed very low or negligible activity as catalysts in ethylene polymerization after activation with an excess of MAO. No time-dependent aggregation was observed for **13**, in contrast with the behavior described above with related dendrimers containing aryloxy units derived from eugenol or 4-allyl-2,6-dimethoxyphenol ligands.

3. Conclusions

In conclusion, in the cases of systems having $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]$ as peripheral unit in *para* position to

the aliphatic substituent, the presence of *ortho*-OMe group in the aryloxy ligand afforded polyethylene of high molecular weights and low polydispersity indistinctly if monometallic or metallodendrimers precursors were used. However, the dendritic nature enforced higher crystallinity percentage of the polymer, although for freshly prepared toluene solutions moderate activities were found. Surprisingly, these titanium ended carbosilane dendrimers spontaneously form in toluene time dependent aggregates when eugenol or 4-allyl-2,6-dimethoxyphenol are used as ligand precursors, and after activation with MAO behaved as highly active catalysts. However, when the peripheral units are replaced by $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2]$ or $[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}]$ fragments or 2-allyl-6-methylphenol are incorporated to the periphery of a carbosilane dendrimer, no aggregation was observed upon aging. Therefore, the electronic and/or the steric effects induced by different organometallic units or phenolic ligands have a big influence in the synthesis and catalytic activity of their organometallic derivatives.

4. Experimental

4.1. Reagents and general techniques

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a dry box. Solvents used were previously dried and freshly distilled under argon: toluene from sodium, and chloroform over P_4O_{10} . MAO was obtained from commercial sources (1.5 M toluene solution from Witco) and used as received. Dendrimers [4,5], $[\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2-\text{SiMe}_2\text{H})_4]$ [15] and $[\text{Ti}(\eta^5-\text{C}_5\text{H}_5)\text{Cl}_3]$ [17] were prepared according to reported methods. $[\text{Ti}(\eta^5-\text{C}_5\text{H}_5)_2\text{Cl}_2]$ and $[\text{Zr}(\eta^5-\text{C}_5\text{H}_5)_2\text{Cl}_2]$ were obtained from commercial sources and used as received.

^1H , ^{13}C and ^{29}Si spectra were recorded on a Variant Unity VXR-300. Chemical shifts (δ ppm) were measured relative to residual ^1H and ^{13}C resonances for chloroform- d_1 and benzene- d_6 used as solvents. The ^{29}Si chemical shifts were referenced to external SiMe_4 (0.00 ppm). The integral values of the signals in the ^1H NMR spectra of complexes **5–6** represent only one-fourth of the total amount of hydrogen atoms per molecule. Light scattering measurements have been carried out in a Malvern equipment with an angle of 90° and at $25\text{ }^\circ\text{C}$. The light source is a He/Ne laser with $\lambda = 632.8\text{ nm}$.

4.2. Synthesis of $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_3(\text{CH}_3)-(\text{CH}_2\text{CH}=\text{CH}_2)\}_2\text{Cl}_2]$ (**9**)

A solution of 2-allyl-6-methylphenol (0.43 g, 2.87 mmol) in toluene (20 mL) was slowly added to a

solution of $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ (0.63 g, 2.87 mmol) in toluene (20 mL). The mixture was heated up to 80 °C for 6 h and subsequently stirred at room temperature overnight. The solvent was removed at reduced pressure and the product was washed with hexane to give **9** as a crystalline orange solid (0.89 g, 94%). ^1H NMR (CDCl_3): δ 6.90–7.10 (m, 3H, C_6H_3), 6.71 (s, 5H, C_5H_5), 5.98 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.10 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 3.40 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.29 (s, 3H, $-\text{CH}_3$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 166.0 (C_{ipso} bonded to $-\text{OTi}$), 136.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 128.9 (C_{ipso} bonded to $-\text{CH}_2\text{CH}=\text{CH}_2$), 124.1 (C_{ipso} bonded to $-\text{CH}_3$), 119.2, 120.5, 127.9 (C_6H_3), 120.9 (C_5H_5), 116.0 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 34.0 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 17.5 ($-\text{CH}_3$). Anal. Calc. for $\text{C}_{15}\text{H}_{16}\text{OCl}_2\text{Ti}$: C, 54.42; H, 4.87. Found: C, 54.53; H, 4.60.

4.3. Synthesis of $[\text{Ti}(\text{C}_5\text{H}_5)_2\{\text{OC}_6\text{H}_3(\text{CH}_3)(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}]$ (**10**)

A solution of 2-allyl-6-methylphenol (0.81 g, 5.46 mmol) in THF (20 mL) was added to a solution of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (1.36 g, 5.46 mmol) in THF (20 mL). To this mixture was added a slight excess of NEt_3 (0.84 mL, 6.0 mmol). The reaction mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with toluene (30 mL). This mixture was filtered through Celite to remove $\text{NEt}_3 \cdot \text{HCl}$. The resulting orange solution was evaporated under reduced pressure to give **10** as a dark orange oil (1.62 g, 83%). ^1H NMR (CDCl_3 , 300 MHz, 298 K): δ 6.93–7.00 (m, 3H, C_6H_3), 6.31 (s, 10H, C_5H_5), 5.99 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.03 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 3.28 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.11 (s broad, 3H, $-\text{CH}_3$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 168.1 (C_{ipso} bonded to $-\text{OTi}$), 137.7 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 129.1 (C_{ipso} bonded to $-\text{CH}_2\text{CH}=\text{CH}_2$), 125.16 (C_{ipso} bonded to $-\text{CH}_3$), 120.0, 128.0, 128.9 (C_6H_3), 117.7 (C_5H_5), 116.6 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 34.6 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 18.7 ($-\text{CH}_3$). Anal. Calc. for $\text{C}_{20}\text{H}_{21}\text{OClTi}$: C, 66.59; H, 5.87. Found: C, 66.01; H, 5.78.

^1H NMR (CD_2Cl_2 , 500 MHz, 223 K, two rotamers in a 2/1 ratio): δ 7.0–6.7 (m, 3H, C_6H_3 , overlapping resonances of both rotamers), 6.33 (s, 10H, C_5H_5 , both rotamers), 5.97 and 5.89 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$, minor and major rotamer), 5.16–4.97 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$, overlapping resonances of both rotamers), 3.37 and 3.07 (d, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$, major and minor rotamer), 2.16 and 2.05 (s, 3H, $-\text{CH}_3$, minor and major rotamer).

4.4. Synthesis of $[\text{Zr}(\text{C}_5\text{H}_5)_2\{\text{OC}_6\text{H}_3(\text{CH}_3)(\text{CH}_2\text{CH}=\text{CH}_2)\}\text{Cl}]$ (**11**)

A solution of 2-allyl-6-methylphenol (0.26 g, 1.73 mmol) in THF (20 mL) was added to a solution of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (0.51 g, 1.73 mmol) in THF (20 mL).

To this mixture was added a slight excess of NEt_3 (0.25 mL, 1.91 mmol). The reaction mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with toluene (30 mL). This mixture was filtered through Celite to remove $\text{NEt}_3 \cdot \text{HCl}$. The resulting orange solution was evaporated under reduced pressure to give **11** as a yellow oil (0.64 g, 92%). ^1H NMR (CDCl_3): δ 6.90–7.03 (m, 3H, C_6H_3), 6.34 (s, 10H, C_5H_5), 6.00 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.08 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 3.26 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.15 (s, 3H, $-\text{CH}_3$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 161.6 (C_{ipso} bonded to $-\text{OZr}$), 137.4 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 128.7 (C_{ipso} bonded to $-\text{CH}_2\text{CH}=\text{CH}_2$), 125.2 (C_{ipso} bonded to $-\text{CH}_3$), 119.6, 127.7, 128.7 (C_6H_3), 114.6 (C_5H_5), 113.7 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 34.2 ($-\text{CH}_2\text{CH}=\text{CH}_2$), 18.2 ($-\text{CH}_3$). Anal. Calc. for $\text{C}_{20}\text{H}_{21}\text{OClZr}$: C, 59.45; H, 5.24. Found: C, 58.97; H, 5.18.

4.5. Synthesis of $1\text{G-Si}[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{Me})\}\text{OH}]_4$ (**12**)

$[\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H})_4]$ (0.14 g, 0.31 mmol) and two drops of the poly(dimethylsiloxane) solution of the Karstedt catalyst (3–3.5% Pt) were slowly added to a solution of 2-allyl-6-methylphenol (0.185 g, 1.25 mmol) in THF (5 mL). The resulting mixture was heated up to 70 °C for 7 h and subsequently stirred at room temperature overnight. Then, the solvent was removed at reduced pressure to give **12** as a yellow-brown solid. ^1H NMR (CDCl_3): δ 6.75–6.95 (m, 3H, C_6H_3), 4.59 (s, 1H, $-\text{OH}$), 2.58 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 2.23 (s, 3H, $-\text{CH}_3$), 1.58 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.28 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.56 (m, 6H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ overlapping), -0.61 (s, 6H, $\text{Si}-\text{CH}_3$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 142.9 (C_{ipso} bonded to $-\text{OH}$), 132.1 (C_{ipso} bonded to $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 122.0 (C_{ipso} bonded to $-\text{CH}_3$), 120.5 (C_5H_5), 128.9, 127.7, 124.3 (C_6H_3), 34.7 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 25.5 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 15.5 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 17.5 ($-\text{CH}_3$), 20.1, 18.4, 12.6 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$), -3.20 ($\text{Si}-\text{CH}_3$). ^{29}Si $\{^1\text{H}\}$ NMR (CDCl_3): δ 1.55 (G1-Si), 1.44 (G0-Si). Silicon resonances assigned by $\{^1\text{H}-^{29}\text{Si}\}$ -HMBC experiments. Anal. Calc. for $\text{C}_{60}\text{H}_{100}\text{O}_4\text{Si}_5$: C, 70.25; H, 9.83. Found: C, 69.87; H, 9.45.

4.6. Synthesis of $1\text{G-Si}[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{Me})\}\text{O}]\text{-Ti}(\text{C}_5\text{H}_5)\text{Cl}_2$ (**13**)

A solution of **12** (0.052 g, 0.05 mmol) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ (0.044 g, 0.20 mmol) in toluene (20 mL). The resulting mixture was heated up to 80 °C for 6 h and subsequently stirred at room temperature overnight. The solvent was removed at reduced pressure and the product washed with hexane to give **13** as an orange oil (0.078 g, 89%). ^1H NMR (CDCl_3): δ 6.67 (s, 5H, C_5H_5), 2.56 (m, 2H,

SiCH₂CH₂CH₂Ph), 2.27 (s, 3H, –CH₃), 1.50 (m, 2H, SiCH₂CH₂CH₂Ph), 1.25 (m, 2H, SiCH₂CH₂CH₂Si), 0.54 (m, 6H, SiCH₂CH₂CH₂Si and SiCH₂CH₂CH₂Ph overlapping), –0.07 (s, 6H, –SiMe₂–). ¹³C {¹H} NMR (CDCl₃): δ 166.5 (C_{ipso} bonded to –OTi), 132.2 (C_{ipso} bonded to –CH₂CH₂CH₂Si), 122.2 (C_{ipso} bonded to –CH₃), 120.8 (C₅H₅), 124.1, 127.8, 128.5 (C₆H₃), 34.9 (SiCH₂CH₂CH₂Ph), 25.7 (SiCH₂CH₂CH₂Ph), 15.6 (SiCH₂CH₂CH₂Ph), 17.5 (–CH₃), 12.5, 18.6, 20.3 (SiCH₂CH₂CH₂Si), –3.23 (Si–CH₃). ²⁹Si {¹H} NMR (CDCl₃): δ 1.53 (G1–Si), 1.42 (G0–Si). Anal. Calc. for C₈₀H₁₁₆Cl₈O₄Si₅Ti₄: C, 54.67; H, 6.60. Found: C, 53.85; H, 6.38.

4.7. Synthesis of 1G-Si[(CH₂)₃{C₆H₃(Me)}O]-Zr(C₅H₅)₂Cl]₄ (**14**)

A solution of **12** (0.056 g, 0.055 mmol) in THF (10 mL) was added to a solution of [Zr(C₅H₅)₂Cl₂] (0.064 g, 0.22 mmol) in THF (20 mL). A slight excess of NEt₃ (0.03 mL, 0.23 mmol) was added to this mixture. The reaction mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with toluene (30 mL). This mixture was filtered through Celite to remove NEt₃·HCl. The resulting solution was evaporated under reduced pressure to give **14** as a yellow oil (0.093 g, 83%). ¹H NMR (CDCl₃): δ 6.31 (s, 10H, C₅H₅), 2.52 (m, 2H, SiCH₂CH₂CH₂Ph), 2.28 (s, 3H, –CH₃), 1.48 (m, 2H, SiCH₂CH₂CH₂Ph), 1.23 (m, 2H, SiCH₂CH₂CH₂Si), 0.50 (m, 6H, SiCH₂CH₂CH₂Si and SiCH₂CH₂CH₂Ph overlapping) –0.06 (s, 6H, –SiMe₂–). ¹³C {¹H} NMR (CDCl₃): δ 162.0 (C_{ipso} bonded to –OZr), 133.4 (C_{ipso} bonded to –CH₂CH₂CH₂Si), 122.6 (C_{ipso} bonded to –CH₃), 121.3 (C₅H₅), 123.8, 127.4, 128.6 (C₆H₃), 34.6 (SiCH₂CH₂CH₂Ph), 25.1 (SiCH₂CH₂CH₂Ph), 15.2 (SiCH₂CH₂CH₂Ph), 13.7, 18.2, 20.1 (SiCH₂CH₂CH₂Si), –3.17 (Si–CH₃). ²⁹Si {¹H} NMR (CDCl₃): δ 1.52 (G1–Si), 1.42 (G0–Si). Anal. Calc. for C₈₀H₁₁₆Cl₈O₄Si₅Zr₄: C, 49.77; H, 6.06. Found: C, 49.53; H, 5.82.

4.8. Ethylene polymerization

A 250 mL flask charged with toluene (50 mL) and equipped with a magnetic stirrer was four times evacuated and refilled with pre-dried ethylene gas. Keeping the flask pressurized with ethylene (1 bar) and stirred at room temperature, a toluene solution of methylaluminoxane (MAO, 0.83 mL, 1.5 M) was syringed through a septum. After 5 min, a toluene solution of the fresh or aged precatalyst (0.50 mL, 2.5 mM) was injected into the flask with simultaneous starting of a stopwatch. The polymerization was quenched 10 min later by closing the ethylene feeding, release of the overpressure and addition of acidified methanol (4% v/v HCl). The mixture was stirred for 6 h and the polymer was filtered,

washed with copious amounts of methanol, and dried in an oven to constant weight.

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Articles

Synthesis of Zirconium(IV) Monocyclopentadienyl–Aryloxy Complexes and Their Use in Catalytic Ethylene Polymerization. X-ray Structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}\{2,6\text{-OC}_6\text{H}_3(\text{CH}_3)_2\}_3$

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The complex $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)\text{Cl}_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (**1**) has been prepared by the reaction of the starting material Cp^*ZrCl_3 and 1 equiv of the lithium salt of the phenol compound. The reactions of **1** and the appropriate Grignard reagents afford the alkyl derivatives $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)\text{Me}_2$ (**2**) and $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)(\text{Bz})(\text{Cl})$ (**3**). This and other dimethyl derivatives, namely, $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3\text{Me}_2)\text{Me}_2$ (**4**), $\text{Cp}^*\text{Zr}(\text{O}-2\text{-}^t\text{Bu}-6\text{-MeC}_6\text{H}_3)\text{Me}_2$ (**5**), and $\text{Cp}^*\text{Zr}(\text{O}-2\text{-C}_3\text{H}_5-6\text{-MeC}_6\text{H}_3)\text{Me}_2$ (**6**), can be obtained by reaction of Cp^*ZrMe_3 and the corresponding phenol. When an excess of the less bulky 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$ phenol was used, the completely substituted complex $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3\text{Me}_2)_3$ (**7**) was obtained. The reactivity of $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)\text{Me}_2$ in the insertion process of isocyanide compounds was studied. In all cases, the corresponding η^2 -iminoacyl compounds, $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)(\eta^2\text{-MeC=NR})(\text{Me})$ [$\text{R} = \text{Xy}$ (**8**); ^nBu (**9**), Cy (**10**), $\text{TMB} = 1,1,3,3\text{-tetramethylbutyl}$ (**11**)], were obtained. Similar reactivity was found for $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)(\text{Bz})(\text{Cl})$ and $\text{Cp}^*\text{Zr}(\text{O}-2\text{-}^t\text{Bu}-6\text{-MeC}_6\text{H}_3)\text{Me}_2$. The complexes were characterized by spectroscopic methods, and in some cases, variable-temperature ^1H NMR spectroscopy studies were carried out. In addition, the molecular structure of $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3\text{Me}_2)_3$ has been determined by X-ray diffraction methods. Finally, complexes $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3^t\text{Bu}_2)\text{Cl}_2$ and $\text{Cp}^*\text{Zr}(2,6\text{-OC}_6\text{H}_3\text{Me}_2)_3$ were tested as ethylene polymerization catalysts in the presence of MAO as cocatalyst. While the former complex shows a high activity similar to that found for classical metallocene catalysts, the latter is much less active. The different activities found for these complexes can be explained in terms of the different activation processes.

Introduction

Alkene polymerization by homogeneous metallocene catalysts has been the object of both fundamental and applied studies, especially after it was reported that the presence of partially hydrolyzed trimethylaluminum (MAO: methylalumoxane) has a favorable effect on the process.¹ Development of new “single-site” group 4 catalyst precursors for optimizing polymerization catalysis is one of the most attractive subjects in the field

of organometallic chemistry.² There are many reports regarding this chemistry that involve metallocene derivatives, but few examples of monocyclopentadienyl derivatives bearing aryloxy ligands³ have been reported even though complexes containing titanium as the metal center have been known for a number of years.^{3b} Recently, Nomura and co-workers⁴ described similar

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monocyclopentadienyl derivatives of titanium-containing bulky disubstituted aryloxy ligands. These complexes play an active role in the polymerization reaction of α -olefins, such as ethylene, 1-hexene, or propylene, using MAO as cocatalyst.

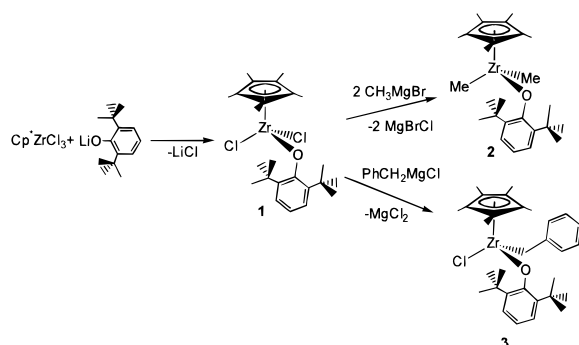
Furthermore, many alkyl or hydride derivatives of group 4 metallocenes are involved in a number of applications that are of great interest in organic synthesis, including carbon monoxide or isocyanide insertions into metal-hydride or metal-alkyl bonds.⁵ This migratory insertion leads to acyl and iminoacyl functions for most of the early d-block metals. In the case of η^2 -iminoacyl derivatives, many examples are known that are more stable than their oxygen counterparts, especially for complexes that do not contain a Cp ligand. In fact, alkyl- or aryloxides of the group 4 metals have been reported⁶ to react with isocyanides, and such reactions have enabled the isolation and characterization of a large number of η^2 -iminoacyl derivatives.

In this paper we wish to extend this chemistry to include the synthesis of zirconium analogues of the type $\text{Cp}^*\text{Zr}(\text{OAr})_n\text{X}_{3-n}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; OAr = aryloxy group; X = halogen, alkyl; $n = 1, 3$). The reactivity of these compounds toward isocyanide insertion and their use in the catalysis of ethylene polymerization, in the presence of MAO as a cocatalyst, were also studied.

Results and Discussion

Synthesis. Complex $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)\text{Cl}_2$ (**1**) was prepared from Cp^*ZrCl_3 by adding 1 equiv of the corresponding lithium phenoxide as a hexane/toluene suspension (see Experimental Section) (Scheme 1).

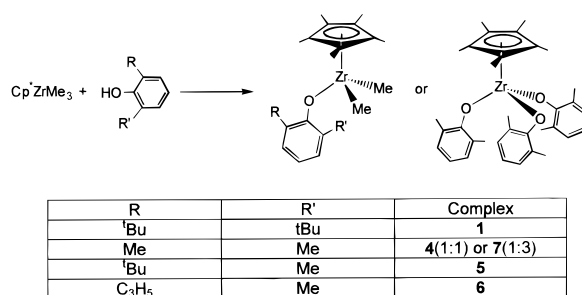
Scheme 1



Compound **1** was obtained as an air-sensitive yellow microcrystalline solid that is soluble in dichloromethane, THF, or toluene, but is scarcely soluble in hexane.

This complex was used as the starting material for the synthesis of new alkyl derivatives (see Scheme 1). Thus, the reaction of complex **1** with 2 equiv of MeMgBr in diethyl ether afforded the complex $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)\text{Me}_2$ (**2**), whereas the reaction with one or more equivalents of BzMgCl afforded the monoalkyl derivative $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)(\text{Bz})(\text{Cl})$ (**3**). The compounds

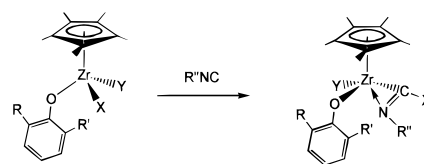
Scheme 2



were isolated as off-white (**2**) or yellow (**3**) microcrystalline solids that are very air-sensitive. It is interesting to note that the analogous complex $\text{Cp}^*\text{Ti}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)\text{Me}_2$ cannot be obtained by the same procedure starting from $\text{Cp}^*\text{Ti}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)\text{Cl}_2$.³ Alternatively, complex **2** could be obtained by the reaction of Cp^*ZrMe_3 with 2,6- $\text{tBu}_2\text{C}_6\text{H}_3\text{OH}$ in hexane. This procedure was extended to other phenols. In this way (see Scheme 2), complexes $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{Me}_2)\text{Me}_2$ (**4**), $\text{Cp}^*\text{Zr}(\text{O-2-tBu-6-MeC}_6\text{H}_3)\text{Me}_2$ (**5**), and $\text{Cp}^*\text{Zr}(\text{O-2-C}_3\text{H}_5\text{-6-MeC}_6\text{H}_3)\text{Me}_2$ (**6**) were obtained in good yields by reacting 1 equiv of Cp^*ZrMe_3 with 1 equiv of the corresponding phenol. Only when an excess of the less bulky 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$ phenol was used was the completely substituted complex $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{Me}_2)_3$ (**7**) obtained.

Due to its relative stability and ease of preparation, complex **2** was chosen to study the reactivity toward isocyanide insertion at the metal-carbon bonds. This complex reacted smoothly with 1 equiv of different isocyanides, namely, XyNC ($\text{Xy} = \text{xylyl} = \text{2,6-Me}_2\text{C}_6\text{H}_3$), nBuNC , CyNC ($\text{Cy} = \text{cyclohexyl}$), or TMBNC ($\text{TMB} = \text{1,1,3,3-tetramethylbutyl}$), to give chiral η^2 -iminoacyl derivatives (see below for characterization) $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)(\eta^2\text{-MeC=NR})(\text{Me})$ [$\text{R} = \text{Xy}$ (**8**); nBu (**9**), Cy (**10**), TMB (**11**)] (see Scheme 3).

Scheme 3



R	R'	R''	X	Y	Complex
tBu	tBu	Xy	Me	Me	8
tBu	tBu	nBu	Me	Me	9
tBu	tBu	Cy	Me	Me	10
tBu	tBu	TMB	Me	Me	11
tBu	tBu	Xy	Bz	Cl	12
tBu	Me	Xy	Me	Me	13

In a similar fashion (see Scheme 3), complexes **3** and **5** reacted with XyNC to give the corresponding η^2 -iminoacyl compounds $\text{Cp}^*\text{Zr}(\text{2,6-OC}_6\text{H}_3\text{tBu}_2)(\eta^2\text{-BzC=NXy})(\text{Cl})$ (**12**) and $\text{Cp}^*\text{Zr}(\text{O-2-tBu-6-MeC}_6\text{H}_3)(\eta^2\text{-MeC=NXy})(\text{Me})$ (**13**). These complexes were synthesized in order to evaluate the different reactivities of the methyl (**2**) and benzyl (**3**) derivatives toward the insertion process and also to assess the influence of an asymmetric bulky aryloxy ligand (**5**) on the chirality of the η^2 -iminoacyl compound.

These complexes were obtained as off-white (**8**, **11**, **12**) microcrystalline solids or as light brown oily materi-

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(6) (a) McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (b) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75.

als (**9**, **10**, **13**), all of which are extremely air-sensitive. A second insertion into the remaining zirconium methyl group was not observed, even when stoichiometries other than 1:1 were tested. When carbon monoxide was used as the reagent in the insertion process, only an intractable mixture of products was obtained.

Characterization. The complexes were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy and elemental analysis (see Experimental Section). The ^1H NMR spectra of **1** and **2** in CDCl_3 show a single peak near 1.4 ppm, which integrates for 18 protons and corresponds to the *tert*-butyl groups of the aryloxy ligand. A similar spectrum was found for compound **4**, which shows a single peak for the methyl group protons of the phenoxy substituent. In addition, peaks corresponding to the Cp^* ligand and aromatic protons of the aryloxy group were observed (see Experimental Section). In contrast, complex **3** shows a very broad peak for the methyl groups of the ^tBu substituents in its ^1H NMR spectrum at room temperature. This behavior indicates that for complexes **1**, **2**, and **4** free rotation about the O–C bond occurs, while this rotation is partially blocked in compound **3**. To study the dynamic behavior in solution, variable-temperature ^1H NMR experiments were performed for these complexes. Complexes **1**, **2**, and **4** show a single peak for the ^tBu or Me groups of the aryloxy ligand, even at low temperatures. In contrast, complex **3** shows splitting of the broad signal at low temperature, and this gives rise to two single peaks at 223 K. When the temperature was raised to 373 K, a single sharp peak was found for complex **3**, indicating that free rotation had been achieved. The coalescence temperature (293 K) and the two site exchange equations⁷ can be used to estimate the value of $\Delta G_c^\ddagger$ to be $14.5 \pm 0.2 \text{ kcal mol}^{-1}$. It is noteworthy that both complexes **5** and **6**, which contain an asymmetric phenoxy group, show a single peak for their zirconium-bonded methyl groups in their ^1H NMR spectra over a wide range of temperatures. This result is in accordance with free rotation of the phenoxy groups even at low temperature, a situation that has previously been described for complexes **1**, **2**, and **4**. Finally, the ^1H NMR spectrum of **7** in C_6D_6 shows a single peak at 2.24 ppm, which integrates for 18 protons and can be assigned to the six equivalent methyl groups of the aryloxy ligands. This equivalence can again be explained in terms of the free rotation of these aryloxy groups around the O–C bonds, even though the metal center is in a more crowded environment in this case. A single-crystal X-ray analysis of compound **7** was carried out in order to provide precise structural details of this compound.

The molecular structure of complex **7** is shown in Figure 1 together with the atomic labeling scheme. The second digit of the phenoxy labels refers to moiety 1, 2, or 3 accordingly. Selected bond distances and angles are summarized in Table 1. The Zr atom coordinates a Cp^* ring in a η^5 and symmetric fashion, as well as three 2,6-dimethylphenoxy oxygen atoms. The complex presents a three-legged piano stool coordination and can also be described as pseudo-tetrahedral if the centroid of the Cp^* ring is considered as occupying one coordination site. The 2,6-dimethylphenoxy ligand **2** lies roughly on

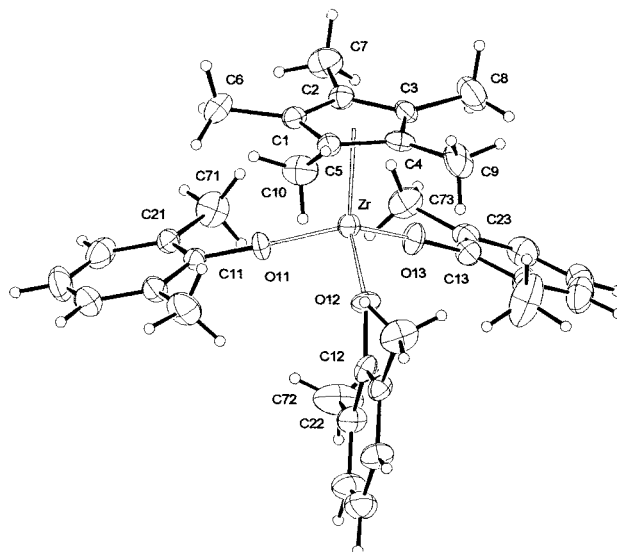


Figure 1. ORTEP drawing of **7**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **7**

Zr–O(11)	1.940(4)	Zr–C(3)	2.531(6)
Zr–O(12)	1.947(4)	Zr–C(4)	2.516(7)
Zr–O(13)	1.950(4)	Zr–C(5)	2.523(7)
Zr–CE ^a	2.220(7)	O(11)–C(11)	1.355(7)
Zr–C(1)	2.525(7)	O(12)–C(12)	1.359(6)
Zr–C(2)	2.541(7)	O(13)–C(13)	1.350(7)
O(11)–Zr–O(12)	103.29(16)	O(13)–Zr–CE	113.0(2)
O(11)–Zr–O(13)	105.82(17)	C(11)–O(11)–Zr	167.5(4)
O(12)–Zr–O(13)	103.54(16)	C(12)–O(12)–Zr	155.3(4)
O(11)–Zr–CE	112.6(2)	C(13)–O(13)–Zr	166.1(5)
O(12)–Zr–CE	117.4(2)		

^a CE is the centroid of the cyclopentadienyl ring

a pseudo mirror plane passing through the Zr atom, the centroid, and the C(2) and C(7) carbon atoms of the cyclopentadienyl ring. The phenoxy ligand **2** is quasi-orthogonal [$83.2(3)^\circ$], and the other two ligands are nearly parallel to the pentatomic ring [$16.6(2)^\circ$ and $22.3(2)^\circ$ for **1** and **3**, respectively]. The O(11)O(12)O(13) plane is almost parallel to the Cp ring [$2.4(2)^\circ$]. Owing to the orientation of the three phenoxy ligands, an enlargement of the O(11)–Zr–O(13) and CE–Zr–O(12) bond angles is observed due to the existence of steric hindrance between the C(71) and C(73), the C(82) and C(9), and the C(82) and C(10) methyl carbon atoms. The two phenoxy ligands related by the pseudo mirror plane show a Zr–O–C bond angle of nearly 180° [$167.5(4)^\circ$ and $166.1(5)^\circ$ for **1** and **3**, respectively], whereas for phenoxy ligand **2** the bond angle is $155.3(4)^\circ$. Despite the difference in the Zr–O–C bond angles, the Zr–O bond distances are practically equal and are shorter than those found in several $[\text{Cp}_2\text{Zr}(\text{O}–\text{Ar})_2]$ or $[\text{Cp}^*_2\text{Zr}(\text{O}–\text{Ar})_2]$ complexes.⁸ As found in these latter complexes, there is no correlation between the Zr–O bond lengths and the Zr–O–C bond angles. Howard et al.⁸ proposed that the M–O–Ar bond angles do not provide a good indication of the extent of M–O π -interactions, and it is most probable that the linearity at the oxygen atom

(7) Abrahams, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; John Wiley and Sons: New York, 1988.

(8) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900, and references therein.

Table 2

complex	$\nu(\text{C}=\text{N})$ (cm^{-1})	δ ^{13}C NMR (ppm) for quaternary iminoacyl carbon atom
8	1567	246.55
9	1580	240.62
10	1589	238.39
11	1580	237.84
12	1597	242.37
13	1585	239.62

is attributable mainly to steric interactions.^{9,10} A comparison with other Zr(IV) complexes containing only one η^5 -coordinated Cp ring was not possible because, after a bibliographic search on the Cambridge Structural Database, we believe that compound **7** is the first example of this type of complex to be structurally characterized. In any case, on the basis of the short Zr–O distances we can propose a strong interaction between the metal center and the surrounding oxygen atoms.

The migratory insertion of alkyl groups toward isocyanide ligands allows the introduction of iminoacyl groups, which are present in different coordination modes. In fact, for high-valent oxophilic early transition metals, the iminoacyl group typically adopts a η^2 -coordination mode through both the nitrogen and the carbon atoms.¹¹ Similarly, a η^2 -coordination mode was proposed for the iminoacyl ligand in complexes **8–13** on the basis of their IR and ^{13}C NMR spectra. In fact, these complexes show characteristic¹¹ $\nu(\text{C}=\text{N})$ stretching vibrations at ca. 1580 cm^{-1} . In addition, iminoacyl quaternary carbon atoms resonate at ca. 240 ppm (see Table 2).

These complexes contain a chiral center at the zirconium atom, and this results in diastereotopic groups in **9–12**, as shown by the NMR spectra (see Experimental Section). In fact, the ^1H NMR spectrum of **9** shows a complex spin system for the hydrogen atoms of the *n*-Bu group, of the type $AA'BB'CC'X_3$; complex **10** shows broad multiplets for the hydrogen atoms of the cyclohexyl group; in complex **11** the methyl groups in position 1 of the TMB group also appear to be diastereotopic, and the $-\text{CH}_2-$ group in position 2 leads to a broad peak; finally, in complex **12** the presence of a diastereotopic group in the benzyl substituent of the iminoacyl ligand is also observed.

A remarkable feature of the ^1H NMR spectra of these iminoacyl complexes at room temperature is the difference observed in the peaks assigned to the *tert*-butyl groups of the aryloxy ligand. Whereas complexes **9** and **10** both show a single peak, integrating for 18 protons, complexes **8** and **12** show two peaks, both of which integrate for 9 protons, and complex **11** displays a very broad peak in this region of the spectrum. In addition, complexes **8** and **12** show two different peaks for the methyl groups of the xylyl moiety. To explain these features, we propose that in complexes **8**, **11**, and **12** the rotation of the phenoxy group about the O–C bond is partially or totally blocked at room temperature,

Table 3. Activity in Ethylene Polymerization

complex	Al/Zr	<i>T</i> ($^{\circ}\text{C}$)	activity (kg PE/mol Zr·h·bar)
1 ^a	499	29	2440
	503	40	2930
	505	58	2170
	1093	29	4260
	1504	29	4030
	1083	40	3910
	1509	40	2770
7 ^b	1500	25	3260
	499	25	28
	1537	25	25
	1026	25	27
	508	35	34
	508	50	74
	2000	25	5260
$\text{Cp}_2\text{ZrCl}_2^c$	2000	25	5260
$\text{Cp}^*\text{ZrCl}_3^d$	1500	24	82
$\text{Cp}^*\text{Ti}(\text{Cl})_2(\text{O}-2,6\text{-iPrC}_6\text{H}_3)^e$	2000	60	1240

^a Experimental conditions: *P*(ethylene) = 3.5 bar; 300 mL of toluene; *t* = 2.5 min. ^b Experimental conditions: *P*(ethylene) = 3.5 bar; 300 mL of toluene; *t* = 45 min. ^c Experimental conditions: *P*(ethylene) = 1 bar; 300 mL of toluene; *t* = 8 min. ^d Experimental conditions: *P*(ethylene) = 3.5 bar; 300 mL of toluene; *t* = 45 min. ^e From ref 4.

whereas in complexes **9** and **10** this rotation is free. To confirm this behavior, a variable-temperature ^1H NMR study was carried out using toluene-*d*₈ as the solvent. Complexes **8** and **12** do not show any equivalence of the *tert*-butyl groups even at 373 K. In contrast, complexes **9** and **10** show a single peak at temperatures as low as 183 K. Complex **11** shows, at 203 K, two peaks corresponding to two inequivalent *t*Bu groups. When the temperature was raised to 273 K, the peaks coalesced, and at 373 K, a single peak was observed. The $\Delta G_c^\ddagger$ value for the rotation process was estimated to be 14.2 ± 0.2 kcal mol^{−1}, which is similar to that found previously for the blocked rotation of the phenoxy group in complex **3** (see above). This blocked rotation could be due to the steric hindrance caused by the bulky iminoacyl nitrogen substituent (e.g., Xy, TMB) acting on the aryloxy group.

As previously mentioned, the presence of a chiral center allowed us to prepare an iminoacyl complex (**13**) with a second center of asymmetry in the phenoxy group. The aim of this was to observe the two possible diastereoisomers in the NMR spectra. In fact, complex **13** has, in addition to the zirconium chiral center, a phenoxy ligand with two different groups at the 2 and 6 positions. If the rotation of the phenoxy group is blocked, as discussed for complexes **8** and **12**, it would be possible to detect two rotameric diastereoisomers. Unfortunately, this rotation was not blocked even at 183 K, as was the case for the parent complex **5**. However, a broadening of the signals corresponding to the 2-*t*Bu and 6-Me substituents was observed at this temperature, indicating that the rotation is beginning to be blocked, and thus the two isomers would be observable.

Catalytic Activity in Ethylene Polymerization Processes. The catalytic activity in ethylene polymerization of the aryloxy derivatives **1** and **7**, in association with MAO, was studied, and the results are explained in terms of the influence of the number of the substituents on the activity. Polymerization reactions were carried out in the temperature range 25–55 $^{\circ}\text{C}$ and at several Al/Zr molar ratios. The results are summarized in Table 3. For comparison, the results obtained by us

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(11) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, 88, 1059.

in the presence of the classical $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system or the monocyclopentadienylzirconium precursor, Cp^*ZrCl_3 ,¹² under similar conditions are also reported.

The activity of both new catalytic systems depends on the Al/Zr ratio, but this effect was much more pronounced for the system based on complex **1**. In this case, the polymerization activity reaches a maximum at an Al/Zr ratio near 1000 and then remains constant or decreases slightly, depending of the reaction temperature. It can be seen from the results in Table 3 that, at a constant Al/Zr ratio, increasing the temperature up to 40 °C leads to an increase in the polymerization rate. This is due to the increase of the propagation rate with temperature. At higher temperatures a decrease in the activity was observed, and this is probably related to the thermal instability of the active species. This is common behavior for the metallocene systems, and the optimal temperature for each system depends on the balance between the propagation rate and the thermal instability.

For instance, the polymerization activity of the system based on complex **7** was still increasing at the highest temperature used (i.e., 50 °C).

In any case, it was also found that polymerization activity of complex **1** was much higher than that observed for complex **7** (almost 100 times) and also than that of the previously described analogous titanium compound,⁴ $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)$, or the precursor, Cp^*ZrCl_3 . In contrast, the activity was on the same order as that of the known $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system (see Table 3).

The stability of complex **7** could explain the different deactivation rate found and the decrease of activity observed for the more thermally unstable system based on complex **1**.

Conclusions

Monocyclopentadienyl–aryloxy derivatives of zirconium can be easily prepared by the reaction of the appropriate monocyclopentadienyl zirconium trichloride or trialkyl precursors and lithium phenoxide or phenol. Alkyl derivatives undergo insertion of one isocyanide molecule into a zirconium–carbon bond, giving rise to the corresponding chiral η^2 -iminoacyl compounds. Similar reactivity was found for methyl or benzyl zirconium derivatives. The dynamic behavior of some of these complexes was studied by means of variable-temperature ^1H NMR studies. The dichloride and triphenoxy complexes **1** and **7** catalyze ethylene polymerization in the presence of MAO as cocatalyst. Complex **1**, $\text{Cp}^*\text{Zr}(\text{O}-2,6\text{-tBu}_2\text{C}_6\text{H}_3)\text{Cl}_2$, was found to be more active by 100 times than the trisubstituted complex **7**, $\text{Cp}^*\text{Zr}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_3$, and 10 times more active than similar titanium complexes described previously.

Experimental Section

General Procedures. All reactions were carried out using Schlenk techniques or a glovebox (model VAC HE-2). Solvents were distilled from the appropriate drying agents and deoxygenated prior to use. Complexes Cp^*ZrCl_3 and Cp^*ZrMe_3 were prepared by literature procedures.¹² Different phenols and

isocyanides were purchased from Aldrich and Fluka, stored over molecular sieves, and deoxygenated before use.

^1H and ^{13}C NMR spectra were obtained on a 300 Unity Varian spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in parts per million relative to SiMe_4 . IR spectra of iminoacyl derivatives were obtained in the region 500–4000 cm^{-1} using an FT-IR Nicolet Magna Spectra spectrophotometer.

Synthesis of $\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_3(\text{C}(\text{CH}_3)_3)_2)\text{Cl}_2$ (1**).** To a solution of 2,6-di-*tert*-butylphenol (3.10 g, 15.02 mmol) in 50 mL of hexane was added a 1.6 M solution of $n\text{BuLi}$ in hexane (9.38 mL, 15.02 mmol). A cloudy white precipitate was obtained immediately. After 2 h of reaction, the liquor was decanted and the precipitate was filtered off, washed with 50 mL of hexane, and dried in vacuo. The solid was mixed with Cp^*ZrCl_3 (5.00 g, 15.02 mmol), and the mixture was suspended in hexane/toluene (1:1) and stirred, at room temperature, for 4 h. The yellow suspension obtained was dried in vacuo, and the residue was extracted with 250 mL of hexane. The volume of the solution was reduced to 25 mL, and it was cooled to -20 °C for 24 h. Complex **1** was obtained as a light yellow microcrystalline solid (50%). ^1H NMR (300 MHz, C_6D_6): δ 1.41 (s, 18H, tBu), 2.09 (s, 15H, Cp^*), 6.87 (t, $J = 7.93$ Hz, 1H, H4), 7.21 (d, $J = 7.93$ Hz, 2H, H3 and H5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 12.57 (Cp^*), 31.85 ($\text{C}(\text{CH}_3)_3$), 35.27 ($\text{C}(\text{CH}_3)_3$), 120.98 (C4), 124.83 (C3 and C5), 127.78 (Cp^*), 139.23 (C2 and C6), 160.76 (C1). Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{O}_3\text{Cl}_2\text{Zr}$: C, 57.35; H, 7.22. Found: C, 57.60; H, 7.46.

Synthesis of $\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_3(\text{C}(\text{CH}_3)_3)_2)(\text{CH}_3)_2$ (2**).** **Method A.** To a solution of Cp^*ZrMe_3 (0.30 g, 1.10 mmol) in 10 mL of hexane was added a solution of 2,6-di-*tert*-butylphenol (0.19 g, 0.94 mmol) in 5 mL of hexane at room temperature. After stirring for 4 h, the solvent was removed in vacuo and the residue was extracted with 10 mL of pentane and cooled at -30 °C for 24 h. Complex **2** was obtained as a white microcrystalline solid (91% yield).

Method B. To a solution of $\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_3\text{tBu}_2)\text{Cl}_2$ (0.29 g, 0.57 mmol) in 25 mL of diethyl ether, at -80 °C, was added 0.38 mL (1.14 mmol) of a solution of MeMgBr in diethyl ether. The mixture was stirred for 6 h at room temperature. The solvent was removed under vacuum, the residue was extracted with 30 mL of hexane, and, after filtration, the solvent was evaporated to afford a white solid (95% yield). ^1H NMR (300 MHz, C_6D_6): δ 0.39 (s, 6H, ZrMe), 1.42 (s, 18H, tBu), 1.75 (s, 15H, Cp^*), 6.89 (t, 1H, $J = 7.81$ Hz, H4), 7.29 (d, 2H, $J = 7.81$ Hz, H3 and H5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 11.60 (Cp^*), 31.71 ($\text{C}(\text{CH}_3)_3$), 35.22 ($\text{C}(\text{CH}_3)_3$), 45.37 (ZrMe), 120.19 (C3 and C5), 120.66 (C4), 125.20 (Cp^*), 139.11 (C2 and C6), 161.62 (C1). Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{OZr}$: C, 67.62; H, 9.17. Found: C, 67.18; H, 9.87.

Synthesis of $\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_3(\text{C}(\text{CH}_3)_3)_2)(\text{CH}_2\text{Ph})(\text{Cl})$ (3**).** To a solution of $\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_3(\text{C}(\text{CH}_3)_3)_2)\text{Cl}_2$ (0.34 g, 0.68 mmol) in 25 mL of diethyl ether, at -80 °C, was added 0.68 mL (0.68 mmol) of a solution of PhCH_2MgCl in diethyl ether. The mixture was allowed to react at 25 °C for 6 h. The solvent was removed under vacuum, and the yellow oily residue was extracted with 40 mL of hexane. After filtration, the solution was concentrated to 10 mL and cooled at -30 °C overnight to afford complex **3** as a yellow microcrystalline solid (81% yield). ^1H NMR (300 MHz, C_6D_6): δ 1.40 (br s, 18H, tBu), 1.74 (s, 15H, Cp^*), 2.55 (AB spin system, 2H, $J_{\text{AB}} = 11.95$ Hz, CH_2Ph), 6.84 (t, 1H, $J = 7.70$ Hz, H4), 7.20 (m, 5H, CH_2Ph), 7.38 (d, 2H, $J = 7.70$ Hz, H3 and H5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 12.07 (Cp^*), 32.40 ($\text{C}(\text{CH}_3)_3$), 35.60 ($\text{C}(\text{CH}_3)_3$), 72.41 ($\text{CH}_2\text{-Ph}$), 120.84 (C3 and C5, from $\text{C}_6\text{H}_3\text{tBu}_2$), 122.47 (C4, from $\text{C}_6\text{H}_3\text{tBu}_2$), 124.37 (C4, from CH_2Ph), 125.41 (Cp^*), 128.79, 128.94 (C2, C6, C3, C5, from CH_2Ph), 138.60 (C1, from CH_2Ph), 145.20 (C2, C6, from $\text{C}_6\text{H}_3\text{tBu}_2$), 161.28 (C1, from $\text{C}_6\text{H}_3\text{tBu}_2$). Anal. Calcd for $\text{C}_{31}\text{H}_{43}\text{OClZr}$: C, 66.69; H, 7.76. Found: C, 66.37; H, 7.52.

Synthesis of $\text{Cp}^*\text{Zr}(\text{OC}_6\text{H}_3\text{RR}')(\text{CH}_3)_2$ [$\text{RR}' = (\text{CH}_3)_2$ (4**);**

(12) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

R = CH₃, **R'** = C(CH₃)₃ (**5**); **R** = CH₃, **R'** = C₃H₇ (**6**)]. Complexes **4**–**6** were synthesized using the method described for complex **2** (method A) with the corresponding phenol.

4: light brown solid, 95% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.26 (s, 6H, ZrMe), 1.76 (s, 15H, Cp*), 2.19 (s, 6H, C₆H₃Me₂), 6.82 (t, 1H, *J* = 7.61 Hz, H4), 7.10 (d, 2H, *J* = 7.61 Hz, H3 and H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 10.92 (Cp*), 17.54 (C₆H₃Me₂), 38.40 (ZrMe), 119.69 (C3 and C5), 120.46 (C4), 120.69 (Cp*), 128.32 (C2 and C6), 159.10 (C1). Anal. Calcd for C₂₀H₃₀OZr: C, 63.60; H, 8.01. Found: C, 63.25; H, 8.45.

5: white solid, 95% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.33 (s, 6H, ZrMe), 1.49 (s, 9H, ^tBu), 1.79 (s, 15H, Cp*), 2.10 (s, 3H, Me), 6.87 (pt, 1H, *J* = 7.77 Hz, *J* = 7.33 Hz, H4), 7.05 (d, 1H, *J* = 7.77 Hz, H3 or H5), 7.25 (d, 1H, *J* = 7.33 Hz, H3 or H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.23 (Cp*), 19.09 (Me), 30.47 (C(CH₃)₃), 34.93 (C(CH₃)₃), 41.26 (ZrMe), 120.04 (C3 or C5), 120.63 (C3 or C5), 124.96 (Cp*), 128.74 (C4), 128.78 (C2 or C6), 137.52 (C2 or C6), 159.80 (C1). Anal. Calcd for C₂₃H₂₆OZr: C, 65.81; H, 8.64. Found: C, 65.47; H, 8.31.

6: brown oil, 95% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.25 (s, 6H, ZrMe), 1.77 (s, 15H, Cp*), 2.17 (s, 3H, Me), 3.39 (d, 2H, *J* = 6.31, CH₂CH=CH₂), 5.09 (m, 2H, CH₂CH=CH₂), 6.06 (m, 1H, CH₂CH=CH₂), 6.84 (pt, 1H, *J* = 7.93 Hz, *J* = 7.40 Hz, H4), 7.01 (d, 1H, *J* = 7.93 Hz, H3 or H5), 7.07 (d, 1H, *J* = 7.40 Hz, H3 or H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 10.97 (Cp*), 17.79 (Me), 34.91 (CH₂CH=CH₂), 39.25 (ZrMe), 115.77, 119.73 (C3 and C5), 120.85 (Cp*), 127.28 (CH₂CH=CH₂), 127.80 (C4), 128.31 (CH₂CH=CH₂), 128.87, 137.36 (C2 and C6), 158.45 (C1). Anal. Calcd for C₂₂H₃₂OZr: C, 65.45; H, 7.99. Found: C, 65.50; H, 7.67.

Synthesis of Cp*Zr(OC₆H₃(CH₃)₂)₃ (7**).** To a solution of Cp*ZrMe₃ (0.15 g, 0.55 mmol) in 10 mL of hexane was added 2,6-dimethylphenol (0.20 g, 1.66 mmol) in 10 mL of hexane. The mixture was stirred for 3 h to afford a yellow precipitate. The solid was filtered off, washed with 15 mL of hexane, and recrystallized from CH₂Cl₂/hexane to afford complex **7** as a white microcrystalline solid (87% yield). ¹H NMR (300 MHz, C₆D₆): δ 1.93 (s, 15H, Cp*), 2.24 (s, 18H, OC₆H₃Me₂), 6.75 (t, 3H, *J* = 7.33 Hz, H4), 6.93 (d, 6H, *J* = 7.33 Hz, H3 and H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.56 (Cp*), 18.30 (OC₆H₃Me₂), 120.88 (C3 and C5), 122.94 (C4), 126.99 (Cp*), 129.42 (C2 and C6), 159.81 (C1). Anal. Calcd for C₃₄H₄₂O₃Zr: C, 69.22; H, 7.18. Found: C, 69.74; H, 7.08.

Synthesis of Cp*Zr(OC₆H₃RR')(R''C=N_x)(Y) [R = R' = ^tBu, X = Y = Me, R'' = Xy (8**), ⁿBu (**9**), Cy (**10**), TMB (**11**); R = R' = ^tBu, X = CH₂Ph, Y = Cl, R'' = Xy (**12**); R = ^tBu, R' = Me, X = Y = Me, R'' = TMB (**13**)].** To a solution of Cp*Zr(OC₆H₃RR')(X)(Y) (0.60 mmol) in 5 mL of hexane was added a solution of the corresponding isocyanide, RNC (0.60 mmol), in 5 mL of hexane. The solution was stirred at room temperature for 5 h, and the solvent was removed under vacuum. Complexes **8**, **11**, and **12** were obtained as off-white solids after recrystallization from pentane. Complexes **9**, **10**, and **13** were obtained as spectroscopically pure light-brown oily materials after several attempts at recrystallization.

8: 90% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.53 (s, 3H, ZrMe), 1.42 (s, 9H, ^tBu), 1.52 (s, 9H, ^tBu), 1.62 (s, 3H, Me from Xy), 1.86 (s, 15H, Cp*), 2.09 (s, 3H, Me from Xy), 2.01 (s, 3H, MeC=N), 6.90 (m, 4H, H3 and H5, from C₆H₃^tBu₂ and Xy), 7.26 (dd, 1H, *J* = 5.10 Hz, *J* = 4.40 Hz, H4 from C₆H₃^tBu₂ or Xy), 7.30 (dd, 1H, *J* = 4.80 Hz, *H* = 5.60 Hz, H4 from C₆H₃^tBu₂ or Xy). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.92 (Cp*), 18.91, 19.09 (Me from Xy), 22.10 (MeC=N), 32.79 (ZrMe), 31.81, 32.45 (C(CH₃)₃), 35.40, 35.52 (C(CH₃)₃), 118.50, 119.34, 125.30, 125.40, 125.73, 128.19, 128.31 (C3, C4, C5 from C₆H₃^tBu₂ and Xy, and from Cp*), 129.03, 131.14 (C2 and C6 from Xy), 138.51, 139.02 (C2 and C6 from C₆H₃^tBu₂), 144.72 (C1 from Xy), 161.73 (C1 from C₆H₃^tBu₂), 246.55 (C=N). Anal. Calcd for C₃₅H₅₁NOZr: C, 70.89; H, 8.67; N, 2.36. Found: C, 69.42; H, 9.15; N, 2.33.

9: 90% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.56 (s, 3H,

ZrMe), 0.80 (t, 3H, *J* = 7.30 Hz, CH₃(δ), from ⁿBu), 1.15 (m, 2H, CH₂(γ), from ⁿBu), 1.43 (s, 18H, ^tBu₂), 1.60 (m, 2H, CH₂(β), from ⁿBu), 1.81 (s, 15H, Cp*), 2.16 (s, 3H, MeC=N), 3.46 (m, 2H, CH₂(α), from ⁿBu), 6.81 (t, 1H, *J* = 7.80 Hz, H4), 7.25 (d, 2H, *J* = 7.80 Hz, H3 and H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.56 (Cp*), 13.89 (CH₃(δ)), 19.12 (MeC=N), 20.96 (CH₂(γ)), 30.25 (ZrMe), 31.56 (C(CH₃)₃), 31.68 (CH₂(β)), 35.34 (C(CH₃)₃), 48.02 (CH₂(α)), 117.66 (Cp*), 118.82 (C4), 124.93 (C3 and C5), 138.49 (C2 and C6), 162.06 (C1), 240.62 (C=N). Anal. Calcd for C₃₁H₆₁NOZr: C, 68.32; H, 9.43; N, 2.57. Found: C, 68.77; H, 9.28; N, 2.69.

10: 90% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.67 (s, 3H, ZrMe), 1.10 (m, 2H, CH₂(4), from Cy), 1.44 (s, 18H, ^tBu₂), 1.62 (br s, 4H, CH₂(3) and CH₂(5), from Cy), 1.72 (br s, 2H, CH₂(2) or CH₂(6), from Cy), 1.83 (s, 15H, Cp*), 2.01 (br s, 2H, CH₂(1) or CH₂(6), from Cy), 2.18 (s, 3H, MeC=N), 3.81 (s, 1H, CH(1), from Cy), 6.83 (t, 1H, *J* = 7.80 Hz, H4), 7.27 (d, 2H, *J* = 7.80 Hz, H3 and H4). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.64 (Cp*), 18.90 (MeC=N), 24.91 (CH₂(4)), 25.20, 25.24 (CH₂(3) and CH₂(5)), 29.91 (ZrMe), 31.15 (C(CH₃)₃), 32.07, 32.95 (CH₂(2) and CH₂(6)), 35.36 (C(CH₃)₃), 60.28 (CH(1)), 117.74 (Cp*), 118.86 (C4), 124.92 (C3 and C5), 138.54 (C2 and C6), 162.07 (C1), 238.39 (C=N). Anal. Calcd for C₃₃H₅₃NOZr: C, 69.41; H, 9.36; N, 2.45. Found: C, 68.95; H, 9.44; N, 2.72.

11: 90% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.64 (s, 3H, ZrMe), 1.44 (br s, 18H, ^tBu₂), 1.60 (s, 3H, N–C(CH₃)₂–), 1.83 (s, 15H, Cp*), 1.76 (s, 2H, –CH₂–), 2.48 (s, 3H, MeC=N), 6.83 (t, 1H, *J* = 7.69 Hz, H4), 7.27 (d, 2H, *J* = 7.69 Hz, H3 and H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.57 (Cp*), 21.96 (MeC=N), 29.75, 30.58 (N–C(CH₃)₂–), 31.20 (ZrMe), 31.75 (–CH₂C(CH₃)₃), 31.82 (C(CH₃)₃), 31.89 (–CH₂C(CH₃)₃), 35.32 (C(CH₃)₃), 54.19 (–CH₂–), 68.35 (N–C(CH₃)₂–), 117.73 (Cp*), 118.72 (C4), 124.91 (C3 and C5), 138.38 (C2 and C6), 162.07 (C1), 237.84 (C=N). Anal. Calcd for C₃₅H₅₉NOZr: C, 69.94; H, 9.89; N, 2.33. Found: C, 69.53; H, 9.65; N, 2.25.

12: 85% yield. ¹H NMR (300 MHz, C₆D₆): δ 1.41 (s, 9H, ^tBu), 1.61 (s, 9H, ^tBu), 1.76 (s, 3H, Me from Xy), 1.89 (s, 15H, Cp*), 2.02 (s, 3H, Me from Xy), 3.97 (AB spin system, 2H, *J*_{AB} = 14.65 Hz, CH₂Ph), 7.27 (m, 2H, H4). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.92 (Cp*), 19.39, 19.42 (Me from Xy), 32.32, 32.77 (C(CH₃)₃), 35.66, 35.74 (C(CH₃)₃), 44.82 (CH₂Ph), 120.10, 122.64, 125.05, 125.44, 126.00, 127.22, 128.61 (C3, C4, C5 from C₆H₃^tBu₂ and Xy, and from Cp*), 122.84 (C4, CH₂Ph), 128.10, 128.40 (C2 or C6, C3 or C5, CH₂Ph), 134.40 (C1, CH₂Ph), 129.76, 130.49 (C2 and C6, Xy), 138.60, 139.90 (C2 and C6, C₆H₃^tBu₂), 144.37 (C1, Xy), 161.63 (C1, C₆H₃^tBu₂), 242.37 (C=N). Anal. Calcd for C₄₀H₅₂NOClZr: C, 69.68; H, 7.60; N, 2.03. Found: C, 69.30; H, 7.44; N, 1.98.

13: 90% yield. ¹H NMR (300 MHz, C₆D₆): δ 0.51 (s, 3H, ZrMe), 0.89 (s, 9H, –CH₂C(CH₃)₂–), 1.40 (s, 3H, N–C(CH₃)₂–), 1.46 (s, 3H, N–C(CH₃)₂–), 1.51 (s, 9H, ^tBu), 1.73 (AB spin system, 2H, *J*_{AB} = 14.65 Hz, –CH₂–), 1.96 (s, 15H, Cp*), 2.14 (s, 3H, C₆H₃^tBu₂), 2.55 (s, 3H, MeC=N), 6.79 (pt, 1H, *J* = 7.81 Hz, *J* = 7.33 Hz, H4), 7.04 (d, 1H, *J* = 7.33 Hz, H3 or H5), 7.21 (d, 1H, *J* = 7.81 Hz, H3 and H5). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 11.36 (Cp*), 19.29 (C₆H₃^tBu₂), 22.04 (MeC=N), 27.91 (ZrMe), 30.51, 30.81 (N–C(CH₃)₂–), 31.61 (C(CH₃)₃), 31.90 (–CH₂C(CH₃)₂–), 32.06 (–CH₂C(CH₃)₃), 35.02 (C(CH₃)₃), 53.74 (–CH₂–), 67.80 (N–C(CH₃)₂–), 117.46 (Cp*), 118.99, 124.78 (C3 and C5), 127.17 (C4), 128.63, 136.93 (C2 and C6), 160.54 (C1), 239.62 (C=N). Anal. Calcd for C₃₂H₅₀NOZr: C, 68.76; H, 9.56; N, 2.51. Found: C, 68.36; H, 9.73; N, 2.38.

Single-Crystal X-ray Diffraction Experimental Data.

Details of the crystal data and a summary of data collection parameters for compound **7** are given in Table 4. Data were collected on a Philips PW 1100 diffractometer using graphite-monochromated Mo Kα radiation. A set of 24 carefully centered reflections in the range 7.0° < θ < 12.4° was used for determining the lattice constants. No decay was observed during the data collection. The data were corrected for Lorentz and polarization effects. The structure was solved by direct

Table 4. Crystal Data and Structure Refinement for 7

empirical formula	C ₃₄ H ₄₂ O ₃ Zr
fw	589.90
temperature	293(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>
unit cell dimens	<i>a</i> = 15.935(5) Å <i>b</i> = 22.262(8) Å <i>c</i> = 8.645(3) Å β = 91.44(2)°
volume	3066(2) Å ³
Z, calcd density	4, 1.278 Mg/m ³
abs coeff	0.389 mm ⁻¹
<i>F</i> (000)	1240
cryst size	0.18 × 0.25 × 0.28 mm
θ range for data collection	3.03–24.00°
index ranges	–18 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 25, 0 ≤ <i>l</i> ≤ 9
no. of rflns collected/unique	5134/4791 [<i>R</i> (int) = 0.0943]
refinement method	full-matrix least-squares on <i>F</i> ²
no. of data/restraints/params	4791/0/354
goodness-of-fit on <i>F</i> ^{2a}	0.705
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0392, <i>wR</i> 2 = 0.0427
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2111, <i>wR</i> 2 = 0.0731
largest diff peak and hole	0.313 and –0.399 e·Å ⁻³

^a GOOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

methods (SIR-92)¹³ and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on *F*² using the SHELXL-97 program.¹⁴ All the hydrogen atoms were geometrically fixed using the riding model. All calculations were carried out on the Digital AlphaStation 255 of the “Centro di Studio per la Strutturistica Diffattometrica” del CNR, Parma. The programs PARST¹⁵ and ORTEP¹⁶ were also used.

Polymerization Test. Reactions were carried out under a controlled atmosphere. High-purity ethylene (Air Liquide) was purified over 3A and 13A molecular sieves. Methylalumoxane

was used without further purification as received from Witco GmbH. Ethylene polymerizations were carried out in a 1 L glass autoclave reactor. Toluene was used as solvent, and the reaction time, monomer pressure, and the amount of catalyst introduced were chosen carefully in order to avoid mass transfer limitations. In a typical procedure, ethylene was first introduced into the reactor at the polymerization temperature until saturation of toluene was achieved. The prescribed amount of zirconium complex precatalyst and MAO were first mixed and allowed to react during 15 min. The mixture was then introduced into the reaction vessel, in a nitrogen stream, and the polymerization was started. Ethylene pressure and temperature were recorded at different polymerization times. The polymerization rate was calculated by measuring the pressure drop. The use of an ethylene reservoir (14 L volume) ensured a final ethylene pressure drop of less than 5% in order to maintain a constant monomer concentration.

The tests were performed twice, and the results were in well agreement, with differences less than 5%. The average values were showed in Table 3.

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Supporting Information Available: Crystal structure data for **7**, including tables of atomic positional parameters, anisotropic thermal parameters, full listing of bond distances and angles, and hydrogen atomic coordinates. The material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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Synthesis, Characterization, and One-Electron Reduction of Mixed-Cyclopentadienyl/Aryloxyde Titanium Dichlorides

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The synthesis and characterization of a series of titanium dichloride derivatives containing both cyclopentadienyl and various substituted aryloxyde ligands, $[\text{CpTi}(\text{OAr})\text{Cl}_2]$ **10–18** and $[\text{Cp}^*\text{Ti}(\text{OAr})\text{Cl}_2]$ **19, 20**, have been investigated. Compounds **10–18** are formed from the reaction of $[\text{CpTiCl}_3]$ with either 1 equiv of the substituted parent phenol in the presence of excess pyridine or with 1 equiv of the corresponding lithium salt of the substituted parent phenoxide in hydrocarbon solvents. Compounds **13, 14, 16**, and **17** are chiral molecules (a nonresolved *racemic* pair) as a result of the presence of either *ortho*-(1-naphthyl) or *ortho*-(1-tetrahydronaphthyl) substituents on the phenoxide ligands. Titanium dichloride compounds **19** and **20** are formed in the reaction of $[\text{Cp}^*\text{TiCl}_3]$ with the corresponding lithium salts of the substituted parent phenoxides in hydrocarbon solvents. The compounds **11, 13, 14, 15, 16, 18, 19**, and **20** have been subjected to single-crystal X-ray diffraction analysis, and each was shown to possess a pseudo-tetrahedral geometry. The compound $[\text{CpTi}(\text{OC}_6\text{H}_2\text{Np-2-Bu}^t\text{-4,6})\text{Cl}_2]$ (**16**) (Np = 1-naphthyl) reacts with 1 equiv of sodium (mercury amalgam) per titanium to produce the chlorine-bridged titanium dimer $[(\text{OC}_6\text{H}_2\text{Np-2-Bu}^t\text{-4,6})\text{CpTi}\{\mu\text{-Cl}\}_2\text{TiCp}(\text{OC}_6\text{H}_2\text{Np-2-Bu}^t\text{-4,6})]$ (**21**). The solid-state structure of **21** shows that the cyclopentadienyl rings are arranged in a transoid fashion about the $[\text{Ti}\{\mu\text{-Cl}\}_2\text{Ti}]$ core with a Ti–Ti distance [3.336(1) Å] and Cl–Ti–Cl bond angles [92.07(4)°] intermediate between those found in paramagnetic $[\text{Cp}_2\text{Ti}\{\mu\text{-Cl}\}_2\text{TiCp}_2]$ and diamagnetic $[(\text{ArO})_2\text{Ti}\{\mu\text{-Cl}\}_2\text{Ti}(\text{OAr})_2]$.

Introduction.

Titanocene dichloride, $[\text{Cp}_2\text{TiCl}_2]$, first synthesized by Wilkinson and co-workers,¹ has proven to be an incredibly versatile stoichiometric reagent and catalyst precursor in organometallic chemistry. This utility of $[\text{Cp}_2\text{TiCl}_2]$ has led to the subsequent development of a number of related titanocenes such as those that contain a variety of alkyl-, aryl-, and heteroatom-substituted Cp rings attached to the titanium metal center. Other developments include the synthesis of titanocenes that have the two Cp rings linked by a hydrocarbon-, heteroatom-, or mixed hydrocarbon/heteroatom-bridge group and the synthesis of chiral titanocene systems for carrying out asymmetric synthesis and catalysis. It has been shown through these advancements in Cp–ligand modification that the physical, chemical, and reactive properties of the titanocene class of compounds can often be varied and/or controlled.² The success of the titanocenes has also stimulated research into the development of mono-Cp derivatives that are further ligated by a non-Cp group $[\text{Cp}(\text{X})\text{TiCl}_2]$ including the so-called “constrained geometry” systems where the Cp and non-Cp ligands are linked by some sort of bridging group.³

Research in our group has focused on the use of the bis-(aryloxyde) compounds $[(\text{ArO})_2\text{TiCl}_2]$, in which the $[(\text{ArO})_2\text{Ti}]$ unit has an isolobal relationship to the $[\text{Cp}_2\text{Ti}]$ one. Both novel and complementary chemistry has been developed with the aryloxyde systems. Along these lines we wish to report here on our work concerning the synthesis and characterization of a number of compounds of the type $[\text{Cp}(\text{OAr})\text{TiCl}_2]$, where OAr is a *ortho*-substituted achiral or chiral aryloxyde ligand, and the one-electron reduction of these compounds that affords the dimeric titanium compounds $[\text{Cp}(\text{OAr})\text{Ti}\{\mu\text{-Cl}\}_2\text{Ti}(\text{OAr})\text{Cp}]$. Further full papers will focus on the reaction chemistry of these systems, whereas in this work structural comparisons between these new compounds and related metallocene $[\text{Cp}_2\text{TiCl}_2]$ and aryloxyde $[(\text{ArO})_2\text{TiCl}_2]$ systems will be made. Portions of this work including subsequent $[\text{Cp}(\text{OAr})\text{TiCl}_2]$ reactivity have been previously communicated.⁴

Results and Discussion.

Following our successful development of the cyclo-metalation-resistant **1** and **3** and cyclometalation-im-

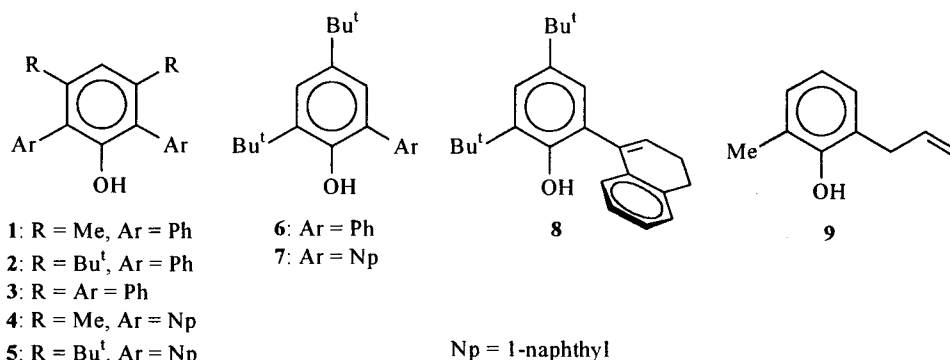
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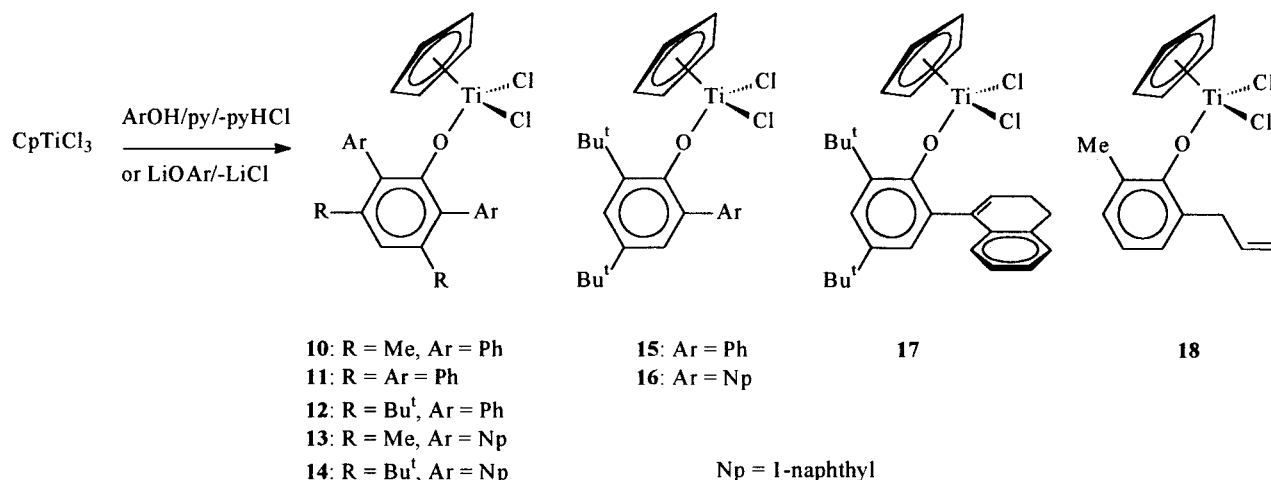
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Scheme 1



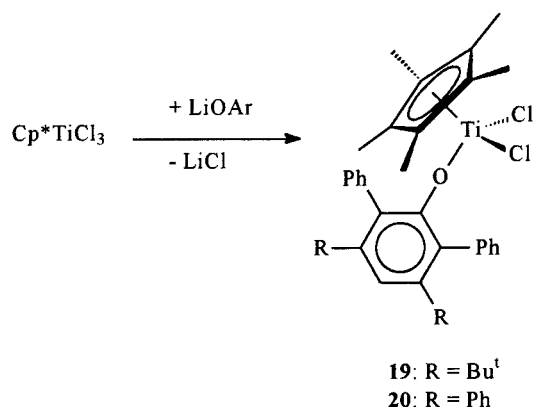
Scheme 2



Scheme 2 aryloxy ligands,⁸ we have since explored the chemistry of the potentially chiral *ortho*-(1-naphthyl)-phenoxides **4**, **5**, and **7** and the related *o*-(1-tetrahydronaphthyl)phenoxide **8** (Scheme 1, Np = 1-naphthyl).⁹ Symmetric **1–3** and **5** and nonsymmetric **6–8** phenols are available from straightforward organic synthetic strategies and have been reported elsewhere, whereas 2-allyl-6-methylphenol (**9**) is commercially available. The synthesis of the chiral compound 2,6-di(1-naphthyl)-3,5-dimethylphenol (**4**) is reported here, and the method for its preparation is identical to that of **5**.

Reaction of phenols **1–4** and **6–9** in the presence of pyridine or the lithium salt of **5** with [CpTiCl₃] affords the compounds **10–18** in good to high yields as orange solids (Scheme 2). Likewise addition of the lithium salt of **2** or **3** to [Cp*TiCl₃] affords the compounds **19** and **20** in moderate yields as red solids (Scheme 3). During one of the syntheses of **11** a few orange chunks of the compound [pyH][CpTiCl₄] were isolated and identified by an X-ray diffraction study (see Experimental Section and Supporting Information for details). The solution NMR spectroscopic properties of **10–20** appear as

Scheme 3



expected with single Cp (Cp* for **19** and **20**) resonances and a single set of aryloxy signals in each case. In the ¹H NMR spectra of **13** and **14** the Cp protons resonate at significantly higher field, δ 5.36 and 5.32, respectively, compared with the δ 5.6–6.0 region found for the other [Cp(OAr)TiCl₂] derivatives. This is a result of the greater diamagnetic shielding of the Cp protons by the presence of the two *ortho*-(1-naphthyl) rings in **13** and **14** that are locked in place by the *meta*-methyl and *meta-tert*-butyl substituents, respectively.⁸

Compounds **11**, **13–16**, and **18–20** have been analyzed by X-ray crystallography (Figures 1–3, Table 2). Full ORTEP views of all of the compounds are contained within the Supporting Information. As expected, each of the titanium dichlorides possess a pseudo-tetrahedral geometry about the metal center. In Table 1 is collected

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Scheme 4

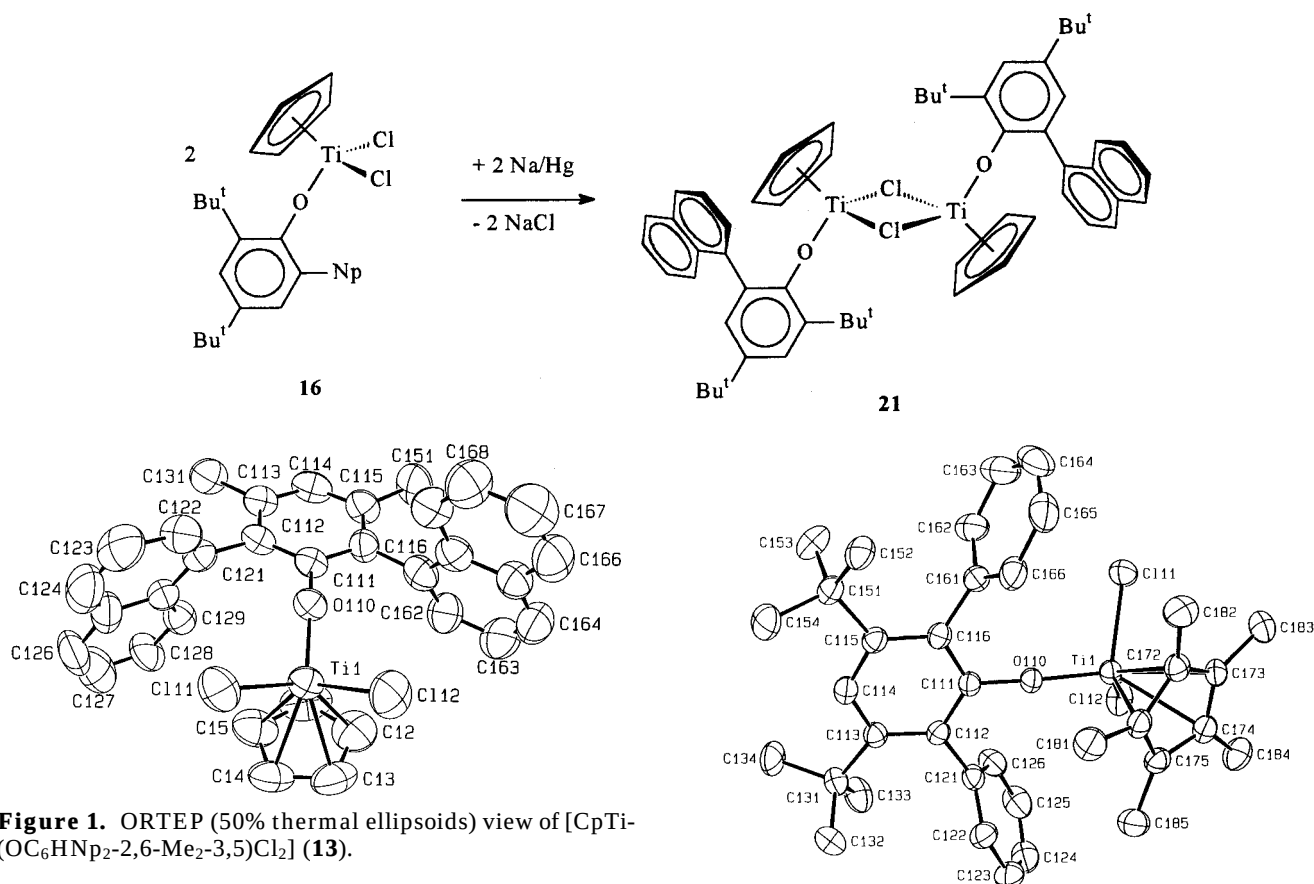


Figure 1. ORTEP (50% thermal ellipsoids) view of $[\text{CpTi}(\text{OC}_6\text{HNP}_2\text{-2,6-Me}_2\text{-3,5})\text{Cl}_2]$ (**13**).

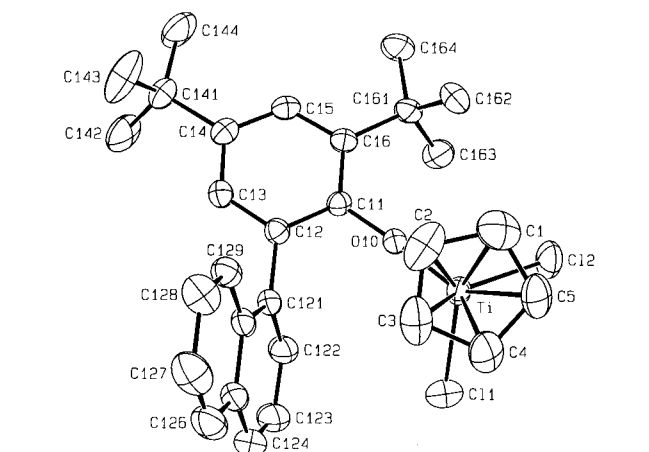


Figure 2. ORTEP (50% thermal ellipsoids) view of $[\text{Cp}^*(\text{Ti}(\text{OC}_6\text{H}_2\text{NP}_2\text{-2-Bu}_2\text{-4,6})\text{Cl}_2)]$ (**16**).

some of the structural parameters for these compounds along with some parameters for related $[(\text{X})(\text{Y})\text{TiCl}_2]$ ($\text{X}, \text{Y} = \text{Cp}, \text{Cp}^*$, or OAr) derivatives.^{10–13} Table 1 is arranged with a focus on the structural effects of replacing Cp ligands with OAr groups on the $[\text{TiCl}_2]$ nucleus with some trends being discerned. The Ti–Cl bond distance decreases significantly as Cp is replaced by OAr, reflecting an increase in electrophilicity at the

Figure 3. ORTEP (50% thermal ellipsoids) view of $[\text{Cp}^*\text{Ti}(\text{OC}_6\text{HPh}_2\text{-2,6-Bu}_2\text{-3,5})\text{Cl}_2]$ (**19**).

metal center. Also noteworthy is the opening of the Cl–Ti–Cl angle with a corresponding closing down of the X–Ti–Y angle upon replacement of Cp by OAr.

Treatment of red **16** with sodium amalgam (1 Na per Ti) leads to a dark solution from which the almost black dimeric species **21** (Scheme 4) can be isolated in low yield upon recrystallization with pentane. The solid-state structure of **21** (Figure 4, Tables 2 and 4) shows a dinuclear compound with a $[\text{Ti}(\mu\text{-Cl})_2\text{Ti}]$ core and terminal aryloxo and Cp groups. The Cp ligands are arranged in a transoid fashion about the core, and a crystallographic inversion center exists in the solid state such that each dimeric unit contains an *ortho*-(1-naphthylphenoxide) ligand of opposite chirality. Table 3 collects structural parameters for **21** along with related $[(\text{X})(\text{Y})\text{Ti}\{\mu\text{-Cl}\}_2\text{Ti}(\text{X})(\text{Y})]$ ($\text{X}, \text{Y} = \text{Cp}$, substituted Cp, Cl, or OAr)^{14–17} compounds. As in the tetrahedral Ti(IV) species in Table 1, the Ti–Cl bond distance decreases as Cp ligands are replaced by OAr groups in the dimeric compounds listed in Table 3. The most interesting parameters in Table 3, however, are the Ti–Ti bond distances. The 3.96(av) and 3.926(3) Å distances in the cyclopentadienyl and methylcyclopentadienyl

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Table 1. Structural Parameters for [(X)(Y)TiCl₂]; X,Y = Cp or ArO

[compound] ^{ref}	Ti—O/Å		X—Ti—Y/deg	Cl—Ti—Cl/deg	O—Ti—Cl/deg	Cp—Ti—Cl/deg
	Ti—Cl/Å	Ti—Cp/Å				
[Cp ₂ TiCl ₂] ¹⁰	2.367(2)	2.058 (av)	131	94		106, 107, 106, 106
[*Cp ₂ TiCl ₂] ¹¹	2.361(1)					
	2.352(1)	2.128 (av)	137	93		105, 105, 104, 104
[11] ^a	2.346(1)					
	2.255(1)	2.016(6)	115	102	106	115
[13] ^a	2.2396(9)				104	114
	2.256(2)	2.010(8)	116	102	105	114
[14] ^a	2.232(2)				103	114
	2.230(2)	2.04(1)	119	102	106	112
[15] ^a	2.244(2)				102	114
	2.2597(8)	2.022(4)	118	99	104	114
[16] ^a	2.2690(8)				105	113
	2.334(2)	2.028(2)	118	101	106	113
[18] ^a	2.321(2)				103	113
	2.2666(8)			102	102	
[19] ^a	2.2609(7)				104	
	2.258(1)	2.052(3)	123	100	104	111
[20] ^a	2.272(1)				104	111
	2.251(1)	2.041(4)	120	101	103	114
[Ti(OC ₆ H ₃ Ph ₂ -2,6) ₂ Cl ₂] ¹²	2.275(1)				105	112
	2.206(1)		109	113	111	
[Ti(OC ₆ H ₃ Me ₂ -2,6) ₂ Cl ₂] ¹³						
	2.192(4)		109	111	109, 109	
	2.211(4)				108, 110	

^a This work.

compounds characterized by Stucky et al. are too long for the presence of any direct metal–metal bonding.¹⁴ In contrast a much shorter distance of 2.9827(7) Å distance is found in the diamagnetic bis(2,6-diphenylphenoxide) species.¹⁷ In the case of the hybrid paramagnetic species **21** the Ti–Ti distance of 3.336(1) Å is intermediate between the previous two molecules and similar to the recently characterized dimeric molecules containing one bulky Cp (C₅Me₄Ph or C₅Bn₅, Bn = CH₂Ph) ligand and one chlorine ligand.¹⁵ In the previously reported 2,6-di-isopropylphenoxide compounds [Cp(OC₆H₃Pr₂-2,6)Ti(μ-Cl)]₂ and [Cp*(OC₆H₃Pr₂-2,6)Ti(μ-Cl)]₂ the Ti–Ti distance were calculated to be 3.19 and 3.36 Å, respectively (Table 3).¹⁶

There has been considerable discussion in the literature as to the nature of the metal–metal interaction within d¹–d¹ dinuclear compounds containing the [Ti(μ-Cl)₂Ti] core. An important class of compounds are the edge-shared bis-octahedral formamidinate complexes [Ti₂{RNC(H)CNR}₂{RNC(H)CNR}₂(μ-Cl)₂] isolated by Cotton et al. (R = C₆H₅, C₆H₄Ph-4)¹⁸ and Gambarotta et al. (R = c-C₆H₁₁).¹⁹ In these diamagnetic compounds the Ti–Ti distances of 2.8890(8), 2.916(3), and 2.942(2) Å, respectively, were taken as indicative of the presence of a metal–metal single bond. In contrast the Ti–Ti distance of 3.740(3) Å in [(PMe₃)₂(Cl)₂Ti(μ-Cl)₂Ti(Cl)₂(PMe₃)₂] indicated the absence of any direct metal–metal interaction.¹⁸ However, an intermediate distance of 3.438(2) Å was found in [(dippe)(Cl)₂Ti(μ-Cl)₂Ti(Cl)₂(dippe)].²⁰ Combining these results with the data obtained in this study, we can form the following conclusions. A Ti–Ti separation of less than 3 Å, e.g., as found in the bis(aryloxy), is strong evidence for the presence of a metal–metal single bond. However, there appears

to be an entire spectrum of Ti–Ti distances (and corresponding metal–metal interaction) possible up to 4 Å for the central [Ti(μ-Cl)₂Ti] core, depending on the nature of the ancillary ligands. In this particular system the concept of the metal–metal bond either being “there” or not is clearly naïve.

Experimental Section

General Details. All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium/benzophenone and stored over sodium ribbons under nitrogen until use. Pyridine was stored over KOH and 4 Å molecular sieves prior to use. The reagents 2-allyl-6-methylphenol, **9**, and BuⁿLi were purchased from Aldrich Chemical Co., Inc., and Cp*TiCl₃ was purchased from Strem; they were used without further purification. The preparation of **1–3**, **5–8**, and [Cp-TiCl₃]¹⁸ has previously been reported. The ¹H and ¹³C NMR spectra were recorded on a Varian Associates Gemini-200, Inova-300, or General Electric QE-300 spectrometer and referenced to protio impurities of commercial benzene-d₆ or deuterated chloroform as internal standards. Elemental analyses and molecular structures were obtained through Purdue in-house facilities.

2,6-Di(1-naphthyl)-3,5-dimethylphenol (4). Following the procedure previously published for **5**, SOCl₂ (1.8 mL, 22 mmol) was added dropwise to a stirred solution of tri(1-naphthyl)bismuth (12 g, 20 mmol) in CH₂Cl₂ at –78 °C. The reaction was stirred 30 min and allowed to warm to room temperature, and the solvent was removed under vacuum. To the remaining powder was added benzene (75 mL), 1,1,2,2-tetramethylguanidine (2 mL 17 mmol), and 3,5-dimethylphenol (0.8 g, 6.4 mmol), and the solution was heated under reflux for 20 h, cooled, and evaporated. The residue was suspended in CH₂Cl₂ and filtered over silica to remove insoluble TMG salts. The filtrate was dried, and the residue was recrystallized from hot heptane, giving 2,6-di(1-naphthyl)-3,5-dimethylphenol (1.2 g, 50%). ¹H NMR (C₆D₆, 30 °C): δ 6.85–7.87 (m, aromatics); 4.48 (s, OH); 1.96 (s, CH₃). Selected ¹³C NMR (C₆D₆, 30 °C): δ 151.0 (O–C); 137.5–123.6 (aromatics); 19.9 (CH₃). HRMS Calcd for C₂₈H₂₂O: 375.1749. Found: 375.1747.

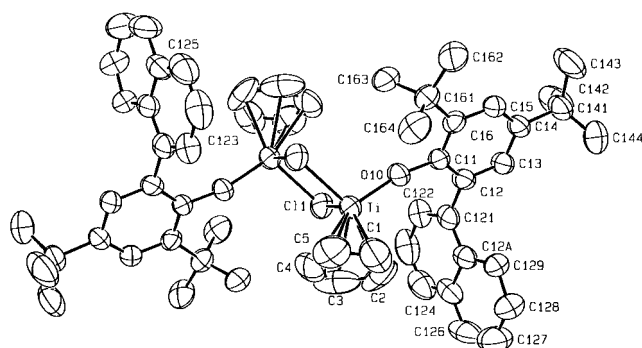
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Table 2. Crystal Data and Data Collection Parameters

	11	13	14	15
formula	C ₃₅ H ₂₆ Cl ₂ OTi	C ₃₃ H ₂₆ Cl ₂ OTi	C ₃₉ H ₃₈ Cl ₂ OTi	C ₂₅ H ₃₀ Cl ₂ OTi
fw	581.40	557.38	641.54	465.32
space group	P2 ₁ /c (No. 14)	P2 ₁ /n (No. 14)	P1 (No. 2)	P2 ₁ /n (No. 14)
a, Å	10.6997(4)	10.6263(5)	10.960(1)	10.6582(2)
b, Å	21.6695(7)	11.5117(6)	11.644(1)	11.9483(4)
c, Å	13.3822(7)	45.870(2)	15.603(1)	19.5208(6)
α, deg	90	90	71.003(7)	90
β, deg	112.640(2)	96.538(3)	76.224(7)	99.957(2)
γ, deg	90	90	63.402(5)	90
V, Å ³	2863.7(4)	5574.6(9)	1673.5(3)	2448.5(2)
Z	4	8	2	4
ρ _{calc} , g cm ⁻³	1.348	1.328	1.273	1.262
temperature, K	296.	296.	296.	296.
radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
R	0.051	0.066	0.076	0.052
R _w	0.125	0.132	0.190	0.129

	16	18	19	20
formula	C ₂₉ H ₃₂ Cl ₂ OTi	C ₁₅ H ₁₆ Cl ₂ OTi	C ₃₆ H ₄₄ Cl ₂ OTi	C ₄₀ H ₃₆ Cl ₂ OTi
fw	515.38	331.10	611.56	651.54
space group	P2 ₁ /c (No. 14)	Pbca (No. 61)	P2 ₁ /c (No. 14)	P2 ₁ /n (No. 14)
a, Å	12.8780(3)	13.1228(5)	12.6364(4)	11.6310(4)
b, Å	11.7288(2)	15.0056(6)	24.0105(9)	12.1794(5)
c, Å	18.3325(4)	15.4237(6)	21.3061(7)	23.7792(6)
α, deg	90	90	90	90
β, deg	105.456(1)	90	92.876(2)	100.320(2)
γ, deg	90	90	90	90
V, Å ³	2668.9(2)	3037.2(4)	6456.3(7)	33.14.0(4)
Z	4	8	8	4
ρ _{calc} , g cm ⁻³	1.283	1.448	1.258	1.306
temperature, K	203.	203.	203.	203.
radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
R	0.045	0.054	0.069	0.061
R _w	0.112	0.109	0.159	0.138

	21	[pyH][CpTiCl ₄]
formula	C ₅₈ H ₆₄ Cl ₂ O ₂ Ti ₂	C ₁₀ H ₁₁ Cl ₄ NTi
fw	959.86	334.92
space group	P2 ₁ /n (No. 14)	P2 ₁ /n (No. 14)
a, Å	12.5923(5)	10.6667(5)
b, Å	12.7390(6)	8.9123(2)
c, Å	17.4609(8)	14.8576(6)
α, deg	90	90
β, deg	109.814(2)	107.3240(15)
γ, deg	90	90
V, Å ³	2635.1(4)	1348.36(16)
Z	2	4
ρ _{calc} , g cm ⁻³	1.210	1.650
temperature, K	296.	173.
radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
R	0.074	0.029
R _w	0.169	0.075

Figure 4. ORTEP (50% thermal ellipsoids) view of [CpTi(OC₆H₂Np-2-Bu^t-2,4,6)Cl]₂ (21).

[CpTi(OC₆HPh₂-2,6-Me₂-3,5)Cl]₂ (10). A sample of [CpTiCl₃] (5.0 g, 22.8 mmol) was dissolved in benzene along with pyridine (2.8 mL, 34.3 mmol). This solution was stirred as 2,6-diphenyl-3,5-dimethylphenol was slowly added (6.2 g, 22.8

mmol). The red mixture was stirred overnight and then filtered to remove pyridine hydrochloride. The filtrate was evacuated to dryness giving a red solid (10.4 g, 84%), which could be recrystallized from benzene/pentane. Anal. Calcd for C₂₅H₂₂Cl₂OTi: C, 65.67; H, 4.85; Cl, 15.51. Found: C, 65.88; H, 4.77; Cl, 15.40. ¹H NMR (C₆D₆, 30 °C): δ 7.19–7.36 (aromatics); 6.79 (s, *para*-H); 5.78 (s, *Cp*); 2.03 (s, *meta*-Me). Selected ¹³C NMR (C₆D₆, 30 °C): δ 164.3 (Ti–O–C); 120.2 (*Cp*); 20.7 (*meta*-Me).

[CpTi(OC₆HPh₂-2,3,5,6)Cl]₂ (11) and [pyH][CpTiCl₄]. A sample of [CpTiCl₃] (2.5 g, 11.5 mmol) was dissolved in benzene along with pyridine (1.5 mL, 18.5 mmol). To this solution was added 2,3,5,6-tetraphenylphenol (4.6 g, 11.5 mmol), the solution was stirred overnight and filtered, and the filtrate was evacuated to dryness, affording a yellow solid (5.2 g, 77%). Dissolving this solid in hot toluene and slow cooling afforded yellow crystals of **2**. Anal. Calcd for C₃₅H₂₆Cl₂OTi: C, 72.31; H, 4.51; Cl, 12.20. Found: C, 72.24; H, 4.53; Cl, 12.10. ¹H NMR (C₆D₆, 30 °C): δ 6.94–7.39 (aromatics); 5.64 (s, *Cp*). Selected ¹³C NMR (CDCl₃, 30 °C): δ 145.3 (Ti–O–C); 120.7 (*Cp*). During one of the syntheses of **11** a few orange chunks were also

Table 3. Structural Parameters for [(X)(Y)Ti(μ -Cl)₂Ti(X)(Y)]; X, Y = Cp or ArO

[compound] ^{ref}	X–Ti–Y/deg	Cl–Ti–Cl/deg	Ti–Cl–Ti/deg	Ti–Cl/Å	Ti–Ti/Å
[Cp ₂ Ti(μ -Cl)] ₂ ¹⁴	132	78	102 101	2.536(2) 2.545(2) 2.545(2) 2.558(2)	3.96(av)
[(C ₅ H ₄ Me) ₂ Ti(μ -Cl)] ₂ ¹⁴	131	79	101 101	2.535(2) 2.566(2) 2.562(2) 2.526(2)	3.926(3)
[(C ₅ Me ₄ Ph)(Cl)Ti(μ -Cl)] ₂ ¹⁵	123	92	88	2.4010(9) 2.2654(9)	3.335(1)
[(C ₅ Bn ₅)(Cl)Ti(μ -Cl)] ₂ ^{15 c}	124	91	89	2.403(2) 2.269(2)	3.374(2)
[21] ^a	125	92	88	2.400(1) 2.406(1)	3.336(1)
[Cp(OC ₆ H ₃ Pr ⁱ ₂ -2,6)Ti(μ -Cl)] ₂ ¹⁶		97	83	2.406(4) 2.397(4)	3.19 ^b
[Cp*(OC ₆ H ₃ Pr ⁱ ₂ -2,6)Ti(μ -Cl)] ₂ ¹⁶		93	88	2.423(3) 2.430(3)	3.36 ^b
[(OC ₆ H ₃ Ph ₂ -2,6) ₂ Ti(μ -Cl)] ₂ ¹⁷	144	102	78	2.3660(9) 2.3761(9)	2.9827(7)

^a This work. ^b Obtained from Cambridge Structural Database. ^c Bn = CH₂Ph.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Cp(OC₆H₂Np-2-Bu^t-4,6)-Ti(μ -Cl)₂Ti(OC₆H₂Np-2-Bu^t-4,6)Cp] (21)

Ti–O(10)	1.817(2)	Ti–Cp	2.036(7)
Ti–Cl(1)	2.400(1)	Ti–Ti	3.336(1)
Ti–Cl(1)	2.406(1)		
Ti–O(10)–C(11)	166.7(2)	O(10)–Ti–Cp	122.2(2)
O(10)–Ti–Cl(1)	102.50(8)	Cl(1)–Ti–Cl(1)	92.07(4)
O(10)–Ti–Cl(1)	103.99(9)	Cl(1)–Ti–Cp	115.4(3)
Ti–Cl(1)–Ti	87.94(4)		

isolated and identified as [pyH][CpTiCl₄] by X-ray diffraction and microanalysis. Anal. Calcd for C₁₀H₁₁Cl₄N₂Ti: C, 35.86; H, 3.31; N, 4.18; Cl, 45.35. Found: C, 35.99; H, 3.29; N, 3.89; Cl, 42.06. ¹H NMR (C₆D₆, 30 °C): δ 5.94 (s, Cp). The Ti–Cl distances vary from 2.3476(5) to 2.4170(5) Å (see Supporting Information).

[CpTi(OC₆HPh₂-2,6-Bu^t-3,5)Cl₂] (12). To a stirred solution of [CpTiCl₃] (0.3 g, 1.4 mmol) in benzene (50 mL) was added lithium 2,6-diphenyl-3,5-di-*tert*-butylphenoxide (0.5 g, 1.4 mmol). The solution immediately became orange and a precipitate formed. The solution was stirred 2 h and filtered, and the solvent was removed under vacuum. The remaining orange powder was recrystallized as X-ray quality crystals from a minimum amount of hot benzene, giving **3** (0.65 g, 82.1%). Anal. Calcd for C₃₁H₃₄Cl₂O₂Ti: C, 68.77; H, 6.33; Cl, 13.10. Found: C, 70.80; H, 7.08; Cl, 12.03. ¹H NMR (C₆D₆, 30 °C): δ 7.72 (s, *para*-H); 7.16–7.30 (m, aromatics); 5.91 (s, Cp); 1.23 (s, CMe₃). Selected ¹³C NMR (C₆D₆, 30 °C): δ 165.8 (Ti–O–C); 147.9, 138.5, 132.9, 131.1, 128.5, 127.8, 121.4 (aromatics); 119.8 (Cp); 37.5 (CMe₃); 33.0 (CMe₃).

[CpTi(OC₆HNP₂-2,6-Me₂-3,5)Cl₂] (13). To a stirred solution of [CpTiCl₃] (1.10 g, 6.0 mmol) in benzene (20 mL) was added 2,6-di(1-naphthyl)-3,5-dimethylphenol (2.25 g, 6.0 mmol) and pyridine (0.5 g). The solution immediately became red and a precipitate formed. The solution was stirred 2 h and filtered, and the solvent was removed under vacuum. The remaining orange powder was recrystallized as X-ray quality crystals from a minimum amount of hexane, giving **13** (2.1 g, 68.6%). Anal. Calcd for C₃₉H₃₈Cl₂O₂Ti: C, 70.99; H, 4.87; Cl, 12.70. Found: C, 71.28; H, 4.69; Cl, 12.98. ¹H NMR (C₆D₆, 30 °C): δ 6.87–7.74 (m, aromatics); 5.36 (s, Cp); 1.92 (s, Me). Selected ¹³C NMR (C₆D₆, 30 °C): δ 165.1 (Ti–O–C); 137.8 135.0, 134.5, 133.4, 129.3, 129.0, 128.8, 128.5, 127.3, 127.0, 125.9, 125.9 (aromatics); 119.7 (Cp); 47.4 (Me).

[CpTi(OC₆HNP₂-2,6-Bu^t-3,5)Cl₂] (14). To a stirred solution of [CpTiCl₃] (50 mg, 0.22 mmol) in benzene (10 mL) was added 2,6-di(1-naphthyl)-3,5-di-*tert*-butylphenol (100 mg, 0.22

mmol) and pyridine (5 drops). The solution immediately became red and a precipitate formed. The solution was stirred 2 h and filtered, and the solvent was removed under vacuum. The remaining orange powder was recrystallized as X-ray quality crystals from a minimum amount of hexane, giving **14** (0.11 g, 78%). Anal. Calcd for C₃₉H₃₈Cl₂O₂Ti: C, 73.02; H, 5.97; Cl, 11.05. Found: C, 72.67; H, 5.96; Cl, 10.93. ¹H NMR (C₆D₆, 30 °C): δ 7.87 (s, *para*-H); 7.13–7.71 (m, aromatics); 5.32 (s, Cp); 1.10 (s, CMe₃). Selected ¹³C NMR (C₆D₆, 30 °C): δ 166.2 (Ti–O–C); 149.1, 136.6, 135.5, 134.2, 130.4, 128.8, 128.7, 128.3, 127.3, 126.3, 126.1, 125.3, 122.4 (aromatics); 119.6 (Cp); 37.9 (CMe₃); 32.8 (CMe₃).

[CpTi(OC₆H₂Ph-2-Bu^t-4,6)Cl₂] (15). A sample of [CpTiCl₃] (4.0 g, 18.2 mmol) was dissolved in benzene along with pyridine (1.5 mL, 18.2 mmol). To this solution was added 2-phenyl-4,6-di-*tert*-butylphenol (5.1 g, 18.2 mmol), causing the solution to immediately to turn red and a precipitate to form. The mixture was stirred for 2 h and then filtered to remove pyridine hydrochloride. The filtrate was evacuated to dryness, affording an orange solid (3.6 g, 42%), which could be dissolved in a minimal amount of benzene and layered with pentane to give red crystals. Anal. Calcd for C₂₅H₃₀Cl₂O₂Ti: C, 64.53; H, 6.50; Cl, 15.24. Found: C, 64.81; H, 6.47; Cl, 15.32. ¹H NMR (C₆D₆, 30 °C): δ 7.20–7.60 (aromatics); 5.70 (s, Cp); 1.63 (s), 1.27 (s, CMe₃). Selected ¹³C NMR (C₆D₆, 30 °C): δ 164.6 (Ti–O–C); 121.1 (Cp); 35.9, 34.7 (CMe₃); 31.5, 30.6 (CMe₃).

[CpTi(OC₆H₂Np-2-Bu^t-4,6)Cl₂] (16). A sample of [CpTiCl₃] (4.0 g, 18.2 mmol) was dissolved in benzene along with 2-naphthyl-4,6-di-*tert*-butylphenol (6.0 g, 18.2 mmol). To this solution was added pyridine (1.5 mL, 18.2 mmol), causing the solution to immediately turn red and a precipitate to form. The mixture was allowed to stand for 30 min and then filtered to remove pyridine hydrochloride. The filtrate was evacuated to dryness, giving a red glassy solid that was dissolved in a minimal amount of pentane. After sitting undisturbed overnight red crystals had formed, which were washed with pentane and dried in vacuo (8.4 g, 89%). Anal. Calcd for C₂₉H₃₂Cl₂O₂Ti: C, 67.59; H, 6.26; Cl, 13.76. Found: C, 67.82; H, 6.37; Cl, 13.59. ¹H NMR (C₆D₆, 30 °C): δ 7.22–8.20 (aromatics); 5.60 (s, Cp); 1.67 (s), 1.25 (s, CMe₃). Selected ¹³C NMR (C₆D₆, 30 °C): δ 165.0 (Ti–O–C); 120.6 (Cp); 36.0, 34.7 (CMe₃); 31.5, 30.7 (CMe₃).

[CpTi(OC₆H₂-{C₁₀H₉}-2-Bu^t-4,6)Cl₂] (17). A sample of [CpTiCl₃] (3.0 g, 13.7 mmol) was dissolved in benzene along with 2-tetrahydronaphthyl-4,6-di-*tert*-butylphenol (5.0 g, 15.0 mmol). This solution was stirred and pyridine (1.7 mL, 21.0 mmol) added, causing the solution to immediately turn red and a precipitate to form. Stirring was continued for 6 h, the

mixture was filtered, and the filtrate was evacuated to dryness, affording a red oil. Recrystallization of the oil with benzene/pentane afforded red crystals (4.2 g, 59%). Anal. Calcd for $C_{29}H_{32}Cl_2OTi$: C, 67.32; H, 6.62. Found: C, 67.31; H, 6.62. ^1H NMR (C_6D_6 , 30 °C): δ 6.92–7.53 (aromatics); 6.09 (t, CH); 5.99 (s, Cp); 2.72 (m), 2.48 (m), 2.21 (m, CH_2CH_2); 1.56 (s), 1.18 (s, CMe_3). Selected ^{13}C NMR (C_6D_6 , 30 °C): δ 165.6 (Ti–O–C); 120.9 (Cp); 35.9, 34.7 (CMe_3); 31.4, 30.7 (CMe_3); 27.9, 23.7 (CH_2CH_2).

[CpTi(OC₆H₃–{C₃H₅}-2-Me-6)Cl₂] (18). A sample of [Cp-TiCl₃] (2.82 g, 12.9 mmol) was dissolved in benzene along with pyridine (1.5 mL, 18.4 mmol). This solution was stirred as 2-allyl-6-methylphenol (1.5 mL, 10.0 mmol) was slowly added. The red solution was stirred overnight and filtered, and the filtrate was evacuated to dryness, affording a red solid (1.4 g, 42%). Addition of minimal pentane to this solid resulted in the formation of X-ray quality crystals. ^1H NMR (C_6D_6 , 30 °C): δ 6.72–6.85 (aromatics); 5.97 (s, Cp); 5.90 (m, $CH=CH_2$); 4.99 (m, $CH=CH_2$); 3.23 (d, CH_2); 2.10 (s, Me). Selected ^{13}C NMR (C_6D_6 , 30 °C): δ 166.0 (Ti–O–C); 124.0 ($CH=CH_2$); 120.5 ($CH=CH_2$); 115.8 (Cp); 34.0 (CH_2); 17.3 (Me).

[Cp*Ti(OC₆HPh₂-2,6-Bu^t-3,5)Cl₂] (19). To a stirred solution of Cp*TiCl₃ (250 mg, 0.86 mmol) in benzene (15 mL) was added 2,6-diphenyl-3,5-di-*tert*-butylphenoxide (320 mg, 0.88 mmol). The solution immediately became red and a precipitate formed. The solution was stirred 2 h and filtered, and the solvent was removed under vacuum. The remaining orange powder was recrystallized as X-ray quality crystals from a minimum amount of hexane (0.28 g, 52.8%). Anal. Calcd for $C_{32}H_{44}Cl_2OTi$: C, 70.70; H, 7.27; Cl, 11.59. Found: C, 70.13; H, 7.32; Cl, 11.96. ^1H NMR (C_6D_6 , 30 °C): δ 7.75 (s, *para*-H); 7.16–7.49 (m, aromatics); 2.09 (s, Cp*); 1.17 (s, CMe_3). Selected ^{13}C NMR (C_6D_6 , 30 °C): δ 163.4 (Ti–O–C); 148.6, 138.8, 134.5, 134.4, 132.8, 131.9, 129.2 (aromatics); 122.0 (Cp*); 38.2 (CMe_3); 33.7 (CMe_3); 13.6 (Cp*).

[Cp*Ti(OC₆HPh₄-2,3,5,6)Cl₂] (20). A solvent-sealed flask was charged with Cp*TiCl₃ (500 mg, 1.73 mmol), the lithium salt of 2,3,5,6-tetraphenylphenol (768 mg, 1.90 mmol), and benzene. This mixture was stirred for 4 h and filtered, and the solvent was removed in vacuo, affording an orange solid that could be recrystallized from benzene/pentane to give orange crystals (470 mg, 42%). Anal. Calcd for $C_{40}H_{36}Cl_2OTi$: C, 73.74; H, 5.57; Cl, 10.88. Found: C, 73.14; H, 5.56; Cl, 10.50. ^1H NMR (C_6D_6 , 30 °C): δ 6.90–7.43 (aromatics); 1.50 (s, Cp*). Selected ^{13}C NMR (C_6D_6 , 30 °C): δ 160.6 (Ti–O–C); 12.3 (Cp*).

[CpTi(OC₆H₂Np-2-Bu^t-4,6)Cl₂] (21). A sample of [Cp*Ti(OC₆H₂Np-2-Bu^t-4,6)Cl₂] (16) (2.0 g, 3.9 mmol) was added to a benzene solution containing sodium (223 mg, 9.7 mmol) as a Hg amalgam. The solution was stirred overnight, filtered to remove Na and Hg salts, and then evacuated to dryness,

affording a dark solid. Pentane was added to this solid and the mixture allowed to rest undisturbed overnight, affording dark red crystals (0.51 g, 14%). Anal. Calcd for $C_{58}H_{64}Cl_2O_2-Ti_2$: C, 72.58; H, 6.72; Cl, 7.39. Found: C, 73.30; H, 6.69; Cl, 6.79.

X-ray Data Collection and Reduction. Full details are contained in the Supporting Information. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo K α radiation (λ = 0.71073 Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.²⁰ An empirical absorption correction using SCALEPACK was applied.²³ Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.²⁴ The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the International Tables for Crystallography.²⁵ Refinement was performed on a AlphaServer 2100 using SHELX-97.²⁶ Crystallographic drawings were done using programs ORTEP.²⁷

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Supporting Information Available: Tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and multiplicities for **11**, **13–16**, and **18–21**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Synthesis of Aryloxo Cyclopentadienyl Group 4 Metal-Containing Dendrimers

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A quantitative procedure for the hydrosilylation of allylic $-\text{SiMe}_3$ protected phenols with Et_3SiH and $\text{Si}-\text{H}$ terminated carbosilane dendrimers of first, second, and fourth generations have been performed to give $n\text{G}-[(\text{CH}_2)_3\{\text{C}_6\text{H}_4-(\text{OMe})_r\text{OH}\}]_m$. The subsequent treatment with $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$, $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$, or $[\text{M}(\text{C}_5\text{H}_5)_2\text{ClX}]$ ($\text{M} = \text{Ti}$, $\text{X} = \text{Cl}$; $\text{M} = \text{Zr}$, $\text{X} = \text{H}$) afforded the corresponding organometallic metallodendrimers.

Introduction

An area of growing interest is the synthesis of metallodendrimers in which the metal has been attached to the surface for generating new inorganic/organic hybrid macromolecules with interesting advantages over both homogeneous and heterogeneous catalysis.¹ On the other hand, Ziegler–Natta polymerization of α -olefins by homogeneous catalysts has been the subject of both fundamental and applied studies, and the development of new “single-site” group 4 catalyst precursors for optimizing polymerization catalysis is one of the most striking subjects in the field of organometallic chemistry.² The combination of these two areas affords cyclopentadienyl group 4 metal derivatives as a family of attractive candidates for the attachment over a dendritic surface, providing in this way model systems for heterogenization of such complexes on, for example, silica supports. A few examples have been reported so far,^{3,4} consisting of bis(cyclopentadienyl) group 4 metals, in which the metallocene units were linked to a carbosilane dendritic skeleton through the ancillary cyclopentadienyl ring.

We have recently reported the synthesis of carbosilane dendrimers with peripheral phenol functionalities that have proved to be useful supports for $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$.⁵ The extension reported here of this methodology to other cyclopentadienyl titanium and zirconium complexes is

also explained by some observations about their catalytic activities.⁶ However, the selectivity of the key reaction affording the phenol-functionalized dendrimers, i.e., the hydrosilylation of allylphenols with the terminal $\text{Si}-\text{H}$ units of carbosilane dendrimers, was limited and an additional study was needed.

Results and Discussion

We have reported⁵ that treatment of 4-allyl-2-methoxyphenol (**1a**; eugenol) or 4-allyl-2,6-dimethoxyphenol (**1b**) with Et_3SiH or $\text{Si}-\text{H}$ terminated dendrimers using Karstedt's catalyst⁷ in THF produced the C-silylated derivatives (hydrosilylation of the olefin fragment) together with variable amounts of the O-silylated products (silylation of the phenol functionality) along with the 2-propenyl isomers of **1**, as a result of competitive isomerization reactions (see Scheme 1). The undesired products (O-silylated and 2-propenyl isomers) could be easily removed using chromatographic techniques. Nevertheless, the overall yield of the reaction was significantly diminished.

To increase the selectivity of the hydrosilylation reaction, we have conducted sets of experiments in which Et_3SiH , 1G-H₄, 2G-H₈, and 4G-H₃₂ have been used in the hydrosilylation reaction of **1a,b**: (i) varying the solvent (THF or toluene), (ii) changing reactant concentrations, (iii) using different catalyst concentrations, and (iv) repeating these experiments while protecting the phenolic function of **1** with the $-\text{SiMe}_3$ group. The percentage of C- and O-silylation was determined by ¹H NMR spectroscopy, as the *o*-methoxy substituent of the phenyl ring is sensitive to the presence of a hydroxy (δ 3.86) or siloxy group (δ 3.78). In a preliminary set of experiments, we observed that solvent polarity does not have an appreciable effect on selectivity and a high concentration of reagents favors the C-silylation versus the two side reactions. In the absence of solvent, the silane dendrimers form a gel and the reaction does not proceed. Thus, unless otherwise

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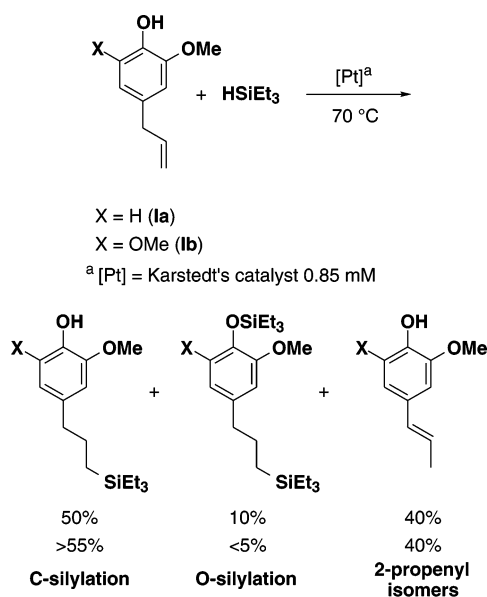
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Scheme 1



^a [Pt] = Karstedt's catalyst (0.85 mM).

stated, the hydrosilylation reactions were carried out in a minimum amount of THF with Karstedt's catalyst (0.8 mM), under an argon atmosphere at 70 °C for 9 h and then at room temperature for 12 h. Under these conditions, Et_3SiH afforded O-silylated products (10–15% for **Ia** and <5% for **Ib**) and 40–50% of isomerized compounds, whereas negligible amounts of O-silylation and a lower percentage of isomerization (15–25%) were found for dendrimers 1G-H₄, 2G-H₈, and 4G-H₃₂. With regard to the catalyst concentration, when it is increased 2- or 3-fold (2.6 mM), the amounts employed above gave an increase of the O-silylation products in the cases of all the silane reagents used and a decrease of the isomerization products, which were negligible for the dendritic silanes. From these results we cannot make a proposal about the nature of the active species in the catalytic cycle, but it seems clear that the polyfunctional nature of the dendrimers strongly favors C-silylation versus O-silylation and isomerization, hence inferring a different mechanism with respect to the monofunc-

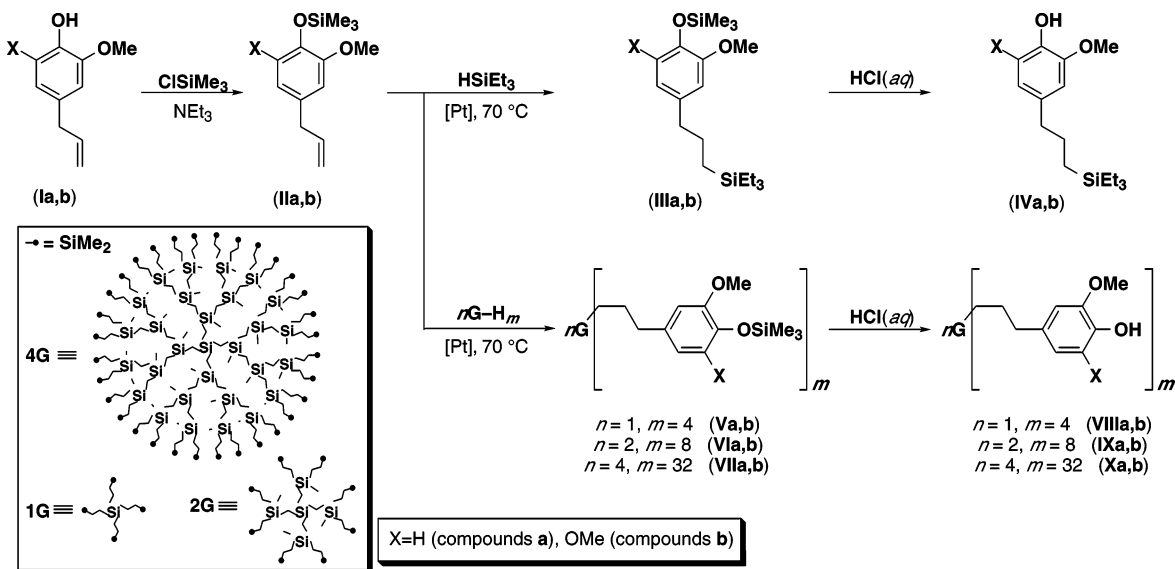
tional Et_3SiH . A similar result was observed by Laine et al. using silsesquioxane silanes.⁸

With the intermediates described above, we carried out the hydrosilylation reactions using $-\text{SiMe}_3$ protected phenols **IIa,b**, which were easily prepared by addition of SiMe_3Cl to the corresponding alcohol in the presence of NEt_3 , and a Karstedt catalyst concentration of 2.6 mM (Scheme 2). As expected, no O-silylation products were found. For Et_3SiH , a dramatic decrease of isomerization reactions occurred, affording **IIIa,b** in high yields. For dendritic silanes, 1G-H₄, 2G-H₈, and 4G-H₃₂, isomerization products were not observed and dendrimers **V–VII** were quantitatively obtained.⁹ The subsequent treatment of these siloxy derivatives with aqueous HCl afforded the previously reported⁵ phenol-terminated carbosilane dendrimers **VIII–X** in 90–95% overall yield after purification by column chromatography.^{5b}

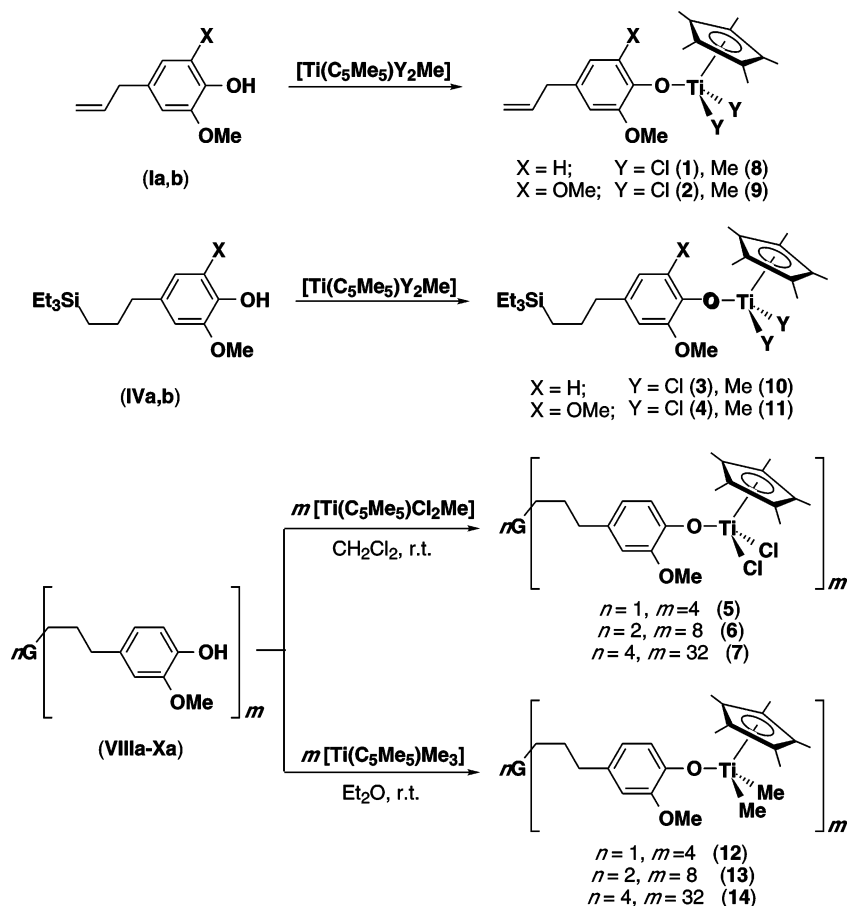
Titanium centers have been successfully incorporated at the surface of the carbosilane dendrimer containing phenol end groups via alcoholysis of a Ti–Cl bond in $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$.⁵ However, this approach is not appropriate for the synthesis of analogous dendrimers containing pentamethylcyclopentadienyl titanium units because of the enhanced stability of the Ti–Cl bond in $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3]$ toward alcoholysis. We have also reported¹⁰ the synthesis in good yield of mononuclear pentamethylcyclopentadienyl aryloxo titanium complexes via reaction of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3]$ with the dilithium salt of different hydroquinones or the lithium salt of eugenol. This second approach may be convenient for early-generation dendrimers but seems to be unsuitable for higher generations because the selectivity of lithiation decreases when the number of phenol groups increases. Here, we describe appropriate synthetic procedures for anchoring chloro and methyl pentamethylcyclopentadienyl titanium fragments to the periphery of phenol-ended dendrimers via reaction of such systems with $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$ or $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$ or bis(cyclopentadienyl) titanium or zirconium units by using $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ or $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{HCl}]$, respectively.

The reaction of monophenolic derivatives **I** and **IV** with $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$ in toluene at room temperature

Scheme 2



Scheme 3



proceeds with evolution of methane to form the corresponding aryloxo complexes **1–4** (see Scheme 3) as red solids in quantitative yields. The same procedure has been used for the synthesis of the corresponding dendrimers. Metathetical replacement of a methyl group by an aryloxo unit is readily achieved when phenol-ended dendrimers **VIIIa–Xa** react with 1 equiv (per phenol group) of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$ in toluene overnight, leading to the new organometallic dendrimers **5–7** (see Scheme 3). These metallodendrimers are obtained as red, moisture-sensitive oils, soluble in aromatic solvents and insoluble in aliphatic solvents.

Aryloxo methyl derivatives have been prepared by reaction of phenol derivatives **I** and **IV** or phenol-ended dendrimers **VIIIa–Xa** with 1 equiv (per phenol group) of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$. In this case, the reaction is carried out in hexane and is complete after 2 h at room temperature, giving the complexes **8**¹⁰ and **9–14** (see Scheme 3). These methyl complexes are soluble in aromatic solvents and in saturated hydrocarbons. They are soluble in chlorinated solvents, but in these solvents Ti–Me bonds are transformed into Ti–Cl bonds. As reported for other aryloxo pentamethylcyclopentadienyl titanium derivatives,¹¹ these methyl derivatives cannot be prepared by methylation of chloro derivatives **1–7**, because methylating reagents such as AlMe_3 and MgClMe react with the Ti–aryloxo bonds of complexes **1–7** to give a mixture of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{MeCl}_2]$, $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$, and aryloxo aluminum or magnesium derivatives.¹²

Phenol-functionalized dendrimers have also been used to support bis(cyclopentadienyl) group 4 complexes at their surface. The preparation of these supported den-

drimers requires different synthetic procedures for titanium and zirconium. Reaction of phenols **Ia**, **IVa**, **VIIIa**, and **IXa** with $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ in the presence of NEt_3 affords monosubstituted aryloxides **15–18** (see Scheme 4). No disubstitution has been observed in any of these reactions, possibly due to steric hindrance at the titanium center relative to zirconium (see below). For the synthesis of mononuclear complexes a light excess of the phenol derivative can be used in order to ensure completion of the reaction. However, in the case of titanium dendrimers an accurate stoichiometry must be used in order to avoid the presence of unsubstituted phenol groups.

In contrast, the reaction of **Ia** with 1 equiv of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ in the presence of 1 equiv of NEt_3 affords a mixture of the starting zirconium precursor together with the mono- and disubstitution aryloxo derivatives, whereas the reaction of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ with 2 equiv of eugenol in the presence of 2 equiv of NEt_3 affords quantitatively the bis(aryloxo) compound **19**. This behavior can be attributed to the larger size of the

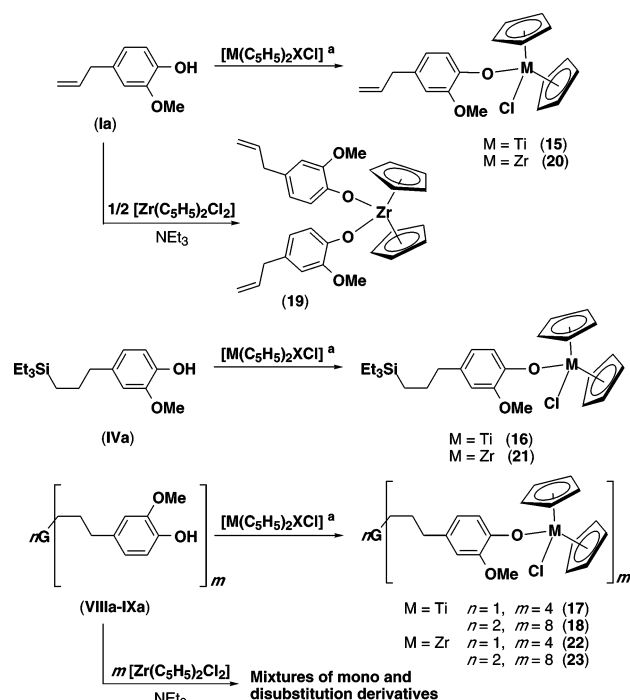
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(9) For spectroscopic data see the Supporting Information.

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(12) For instance, the reaction of **Ib** with AlMe_3 allowed the isolation of an aryloxo aluminum derivative, $\{(\text{AlMe}_2)_2[\mu\{-\{\text{C}_6\text{H}_2(\text{OMe})_2-\text{C}_3\text{H}_5\}\}_2]\}$. ¹H NMR (CDCl_3): δ 6.37 (s, 4H, C_6H_2), 5.70 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.06 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.80 (s, 12H, OMe), 3.30 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), -0.83 (s, 12H, Al–CH₃). ¹³C{¹H} NMR (CDCl_3): δ 147.4 (C_{ipso} bonded to –OMe), 137.4 ($\text{CH}_2\text{CH}=\text{CH}_2$), 131.9 (C_{ipso} bonded to –C₃H₅), 115.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 104.4 (C_6H_2), 56.4 (OMe), 40.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), -9.2 (Al–CH₃).

Scheme 4^a

^a Conditions: M = Ti, X = Cl, toluene as solvent, NEt₃ must be added; M = Zr, X = H, THF as solvent.

zirconium center that allows the entry of a second aryloxo ligand to its coordination sphere.¹³

Nevertheless, we have been able to obtain monosubstituted aryloxo derivatives of zirconium by reaction of phenols **Ia**, **IVa**, **VIIIa**, and **IXa** with 1 equiv of [Zr(C₅H₅)₂HCl] (per phenol group) to give **20–23** in quantitative yield with evolution of dihydrogen (see Scheme 4).

These bis(cyclopentadienyl) titanium and zirconium derivatives are moisture sensitive and in the presence of air decompose, giving the μ -oxo complexes [$\{\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}\}_2(\mu\text{-O})$] (M = Ti,¹⁴ Zr¹⁵), although they can be stored under an inert atmosphere for long time periods. All of them are soluble in chlorinated and aromatic solvents and completely insoluble in saturated hydrocarbons.

The organometallic compounds have been characterized using ¹H, ¹³C, and ²⁹Si NMR spectroscopy and elemental analysis (full details are given in the Supporting Information). For complex **2** the solid-state structure has been determined by X-ray diffraction methods.

The ¹H NMR spectra of some metallodendrimers have shown small peaks of impurities (less than 2%) due to hydrolysis processes or solvent molecules, which were difficult to separate. The NMR spectra of all complexes **1–23** show singlets corresponding to the pentamethylcyclopentadienyl or cyclopentadienyl ligands in the expected region (see the Supporting Information). Methyl groups bonded to titanium appear as singlets in ¹H NMR (0.40 ppm) and in ¹³C NMR (53.6 ppm). From

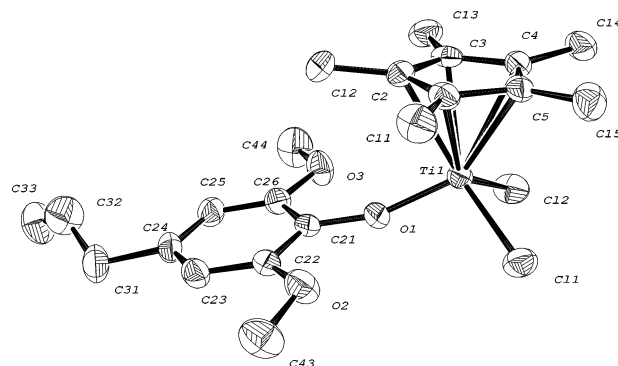


Figure 1. ORTEP (50% thermal ellipsoids) view of [Ti(C₅Me₅)Cl₂{O[C₆H₂(OMe)₂(CH₂CH=CH₂)]}] (**2**). Selected bond lengths (Å) and angles (deg): Ti(1)–O(1) = 1.770(3), Ti(1)–Cl(1) = 2.2661(18), Ti(1)–Cp(1) = 2.026; Cp(1)–Ti(1)–O(1) = 118.9, Ti(1)–O(1)–C(21) = 163.1(3).

these data it could be assumed that substitution of the eugenolate moiety for the 2,6-dimethoxyphenoxide fragment or hydrosilylation of the allyl fragment does not produce significant changes on the electronic density at the metal center.

For complexes **1**, **2**, **8**, **9**, **15**, **19**, and **20**, the allyl group resonances were unambiguously assigned. The ¹H NMR data of the dendritic complexes show, in contrast, the presence of the SiCH₂CH₂CH₂–Ph fragment as the result of an anti-Markovnikov addition of a Si–H bond to the allyl fragment. The resonance patterns for these methylene protons and for the methylene protons of the branches –SiCH₂CH₂CH₂Si– present in the dendrimers are in agreement with the proposed formulation (full details of the assignment of these signals is given in the Experimental Section and the Supporting Information, and a more detailed discussion of this assignment can be found in ref 5b). The carbosilane fragments do not present significant changes, due to the nature and number of the cyclopentadienyl rings or to the presence of a titanium or zirconium metal center. In agreement with this, the ²⁹Si NMR data show no significant changes from the organic dendritic precursors or the metallodendrimers containing [Ti(C₅H₅)Cl₂] units, as was expected.

Single crystals of **2** suitable for X-ray diffraction studies were obtained from a mixture of Et₂O and hexane cooled to –20 °C. An ORTEP drawing of the molecular structure is shown in Figure 1. The Ti–O bond (1.76 Å) and Ti–O–C angle (163.0°) are almost identical with those of other similar monometallic complexes such as {Ti(C₅Me₅)[O(2,6-Me₂C₆H₃)]Cl₂}¹⁶ or an analogue containing the unsubstituted cyclopentadienyl ligand, {Ti(C₅H₅)[O(2,6-ⁱPr₂C₆H₃)]Cl₂}.^{11,17}

In summary, we have developed a synthetic strategy to obtain selectively the C-silylation products of phenols having pendant allyl groups with Si–H terminated dendrimers and allowing the synthesis of phenol-ended carbosilane dendrimers in almost quantitative yields. These dendrimers can be used to anchor different mono- and bis(cyclopentadienyl) complexes of titanium and zirconium through the use of suitable organometallic

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precursors. In all cases, the dendritic framework seems to be chemically inert and spectroscopically invariable to the changes produced in the periphery, while the organometallic unit retains the spectroscopic, and hence chemical, properties of the mononuclear counterparts.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a drybox. Solvents used were previously dried and freshly distilled under argon: tetrahydrofuran from sodium benzophenone ketyl, toluene from sodium, hexane from sodium–potassium, and methylene chloride over P_4O_{10} . Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Ti(C_5Me_5)Cl_3]$,¹⁸ $[Ti(C_5Me_5)Cl_2Me]$,¹⁹ $[Ti(C_5Me_5)Me_3]$,²⁰ and *Gn*-H dendrimers²¹ were prepared according to reported methods.

^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on Varian Unity VXR-300 and Varian 500 Plus instruments. Chemical shifts (δ , ppm) were measured relative to residual ^1H and ^{13}C resonances for chloroform-*d* and benzene-*d*₆ used as solvents, and ^{29}Si chemical shifts were referenced to external $SiMe_4$ (0.00 ppm). The integral values of the signals in the ^1H NMR spectra of dendrimer complexes represent only one-fourth of the total amount of hydrogen atoms. C, H analyses were carried out with a Perkin-Elmer 240 C microanalyzer. Thin-layer chromatography was accomplished using 0.25 mm silica gel plates from Alugram, and chromatography was performed on silica gel (35–70 mesh) for the organic dendrimers.

A selection of synthetic procedures and data are shown; for the rest, see the Supporting Information.

Synthesis of 4G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅Me₅)Cl₂]₃₂ (7). A solution of 4G-[(CH₂)₃{[C₆H₃(OMe)]OH}₃₂] (0.30 g, 2.75×10^{-2} mmol) in CH_2Cl_2 (10 mL) was slowly added to a solution of $[Ti(C_5Me_5)Cl_2Me]$ (0.24 g, 0.88 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred overnight. The solvent was removed at reduced pressure, to obtain a foamy red solid. The product was washed with Et_2O (2×2 mL) to give **7** as a red foamy solid (0.39 g, 75% yield). ^1H NMR ($CDCl_3$): δ 6.84 (m, 8H, C₆H₃), 6.60 (m, 16H, C₆H₃), 3.77 (s, 24H, OMe), 2.52 (m, 16H, SiCH₂CH₂CH₂Ph), 2.16 (s, 120H, C₅Me₅), 1.54 (m, 16H, SiCH₂CH₂CH₂Ph), 1.24 (m, 30H, SiCH₂CH₂CH₂Si), 0.52 (m br, 76H, SiCH₂CH₂CH₂Si and SiCH₂CH₂CH₂Ph overlapping), –0.07 (m br, 69 H, SiMe₂ and SiMe overlapping). ^{13}C NMR ($CDCl_3$): δ 153.4 (C_{ipso} bonded to –OTi), 149.9 (C_{ipso} bonded to –OMe), 138.6 (C_{ipso} bonded to –CH₂), 132.7 (C₅Me₅), 120.6, 120.1, and 113.0 (C₆H₃), 56.3 (OMe), 39.9 (SiCH₂CH₂CH₂Ph), 26.1 (SiCH₂CH₂CH₂Ph), 15.3 (SiCH₂CH₂CH₂Ph), 20.2, 18.9, 18.5, and overlapped signals (Si(CH₂)₃Si), 12.8 (C₅Me₅), –3.2 (SiMe₂), –4.9 (SiMe). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.91 (G4-Si), 1.28 (G3-Si); the rest were not observed. Anal. Calcd for $C_{912}H_{1500}Cl_{64}O_{64}Si_{61}Ti_{32}$: C, 57.64; H, 7.95. Found: C, 56.82; H, 7.70.

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Synthesis of 4G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅Me₅)Me₂]₃₂ (14). A solution of 4G-[(CH₂)₃{[C₆H₃(OMe)]OH}₃₂] (0.30 g, 2.75×10^{-2} mmol) in Et_2O (10 mL) was slowly added to a solution of $[Ti(C_5Me_5)Me_3]$ (0.20 g, 0.88 mmol) in Et_2O (5 mL). The reaction mixture was stirred for 2 h at room temperature. The solvent was removed at reduced pressure to obtain **14** as a brown-yellow oil in quantitative yield (0.48 g). Selected data are as follows. ^1H NMR ($CDCl_3$): δ 0.38 (s, 48H, TiMe₂). ^{13}C NMR ($CDCl_3$): δ 152.3 (C_{ipso} bonded to –OTi), 53.8 (TiMe₂). The rest of the data are almost invariable with respect to compound **7**; see the Supporting Information. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.94 (G4-Si), 1.31 (G3-Si); the rest were not observed. Anal. Calcd for $C_{976}H_{1692}O_{64}Si_{61}Ti_{32}$: C, 66.24; H, 9.64. Found: C, 65.02; H, 9.40.

Synthesis of 2G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅H₅)₂Cl]₈ (18). A solution of 2G-[(CH₂)₃{[C₆H₃(OMe)]OH}₈] (0.10 g, 0.04 mmol) in toluene (10 mL) was slowly added to a solution of $[Ti(C_5H_5)_2Cl_2]$ (0.08 g, 0.32 mmol) in toluene (50 mL). To this mixture was added a slight excess of NEt_3 (50 μ L, 0.36 mmol). The reaction mixture was stirred for 12 h and then filtered through Celite to remove $NEt_3 \cdot HCl$. The resulting red solution was evaporated under reduced pressure to give **18** as a red microcrystalline solid (0.127 g, 79%). ^1H NMR ($CDCl_3$): δ 6.67–6.60 (m, 6H, C₆H₃), 6.32 (s, 20H, C₅H₅), 3.76 (s, 6H, OMe), 2.51 (m, 4H, SiCH₂CH₂CH₂Ph), 1.54 (m, 4H, SiCH₂CH₂CH₂Ph), 1.29 (m, 6H, SiCH₂CH₂CH₂Si), 0.50 (m, 16H, SiCH₂CH₂CH₂Ph and SiCH₂CH₂CH₂Si overlapping), –0.07 (s, 12H, SiMe₂), –0.09 (s, 3H, SiMe). ^{13}C NMR ($CDCl_3$): δ 159.1 (C_{ipso} bonded to –OTi), 145.8 (C_{ipso} bonded to –OMe), 134.9 (C_{ipso} bonded to –CH₂), 125.1, 120.5, and 111.8 (C₆H₃), 117.4 (C₅H₅), 55.9 (OMe), 39.9 (SiCH₂CH₂CH₂Ph), 26.4 (SiCH₂CH₂CH₂Ph), 15.6 (SiCH₂CH₂CH₂Ph), 22.7, 19.1, 18.7, and overlapped signals (Si(CH₂)₃Si), –2.9 (SiMe₂), –4.6 (SiMe). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.87 (G2-Si), 1.19 (G1-Si), 0.77 (G0-Si). Anal. Calcd for $C_{216}H_{308}Cl_8O_{16}Si_{13}Ti_8$: C, 61.88; H, 7.40. Found: C, 61.52; H, 7.46.

Synthesis of 2G-[(CH₂)₃{[C₆H₃(OMe)]O}Zr(C₅H₅)₂Cl]₈ (23). A solution of 2G-[(CH₂)₃{[C₆H₃(OMe)]OH}₈] (0.05 g, 0.02 mmol) in THF (5 mL) was slowly added to a suspension of $[Zr(C_5H_5)_2HCl]$ (0.04 g, 0.17 mmol) in THF (5 mL). The reaction mixture was stirred for 15 min. After hydrogen evolution ceased, the resulting yellow solution was evaporated under reduced pressure, affording quantitatively **23** as a yellow oil (0.088 g). Selected data are as follows. ^1H NMR ($CDCl_3$): δ 6.33 (s, 20H, C₅H₅). ^{13}C NMR ($CDCl_3$): δ 152.6 (C_{ipso} bonded to –OZr), 114.4 (C₅H₅). The rest of the data are almost invariable with respect to those of compound **18**; see the Supporting Information. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.86 (G2-Si), 1.19 (G1-Si), 0.77 (G0-Si). Anal. Calcd for $C_{216}H_{308}Cl_8O_{16}Si_{13}Zr_8$: C, 57.18; H, 6.79. Found: C, 56.92; H, 6.56.

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Supporting Information Available: Text giving experimental procedures and NMR and analytical data of all the complexes, figures giving a selection of ^1H , ^{13}C , and ^{29}Si NMR spectra of titanium and zirconium mononuclear complexes and dendrimers, and tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters of compound **2**; X-ray crystal data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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