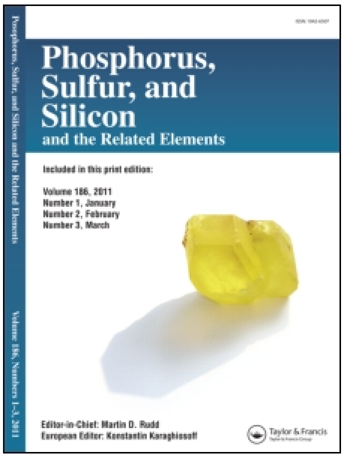

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Metallocenes with Cp Ring-Fused to Chalcogen Heterocycles: Synthesis and Polymerization Results

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Metallocenes with Cp Ring-Fused to Chalcogen Heterocycles: Synthesis and Polymerization Results

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Substituted metallocene ligands containing cyclopentadiene ring fused to either selenophene or benzo[b*]tellurophene were prepared following methods previously developed for analogs containing sulfur. 5-Methyl-4,5-dihydro-cyclopenta[* b*]-selenophen-6-one (**2**) and 3-Methyl-3,4-dihydro-benzo[b]cyclopenta[d]telluraphen-2-one (**7**) (major isomers) were prepared by polyphosphoric acid catalyzed Friedel-Crafts acylation / Nazarov cyclization of methacrylic acid onto selenophene and respectively benzo[*b*]tellurophene. Following reduction of the ketone to alcohol, then dehydration, the chalcogen-containing cyclopentadiene olefins were prepared. The olefins were deprotonated with n-butyllithium followed by either bridging with dichlorodimethylsilane, deprotonation and metallation, or deprotonation and direct metallation. In this manner, isomeric mixtures of –*rac / -meso *dimethylsilanediylbis(η^5-5-Methyl-cyclopenta[b]selenophenyl)zirconium dichloride (**5**) Bis(η^{5-}2-methyl-cyclopenta[b][1]benzotelluraphenyl)zirconium dichloride (**9**) were prepared and characterized. Complexes formed active olefin polymerization catalyst when activated with methylalumoxane. Polymerization results with ethylene and propylene are included.*

Keywords Heterocenes; polypropylene; selenopentalene; tellurapentalene; zirconocene

INTRODUCTION

Rationally designed ligands create the environment for stereo- and regio-controlled olefin polymerizations.[1,2] In recent developments, group 4 metallocene complexes have been made with ligands containing heteroatoms in rings fused to cyclopentadiene (Cp).[3] When activated

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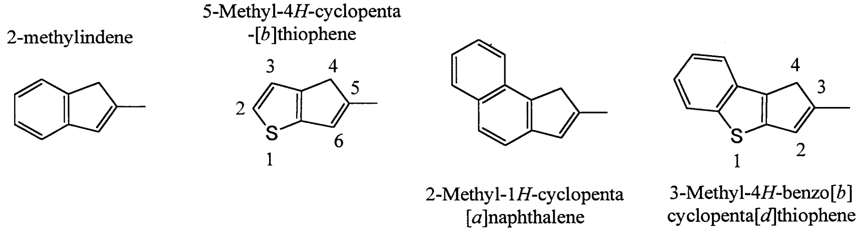
with methylalumoxane (MAO), these complexes polymerize α-olefins at very high rates with regio- and stereo-chemical control.

Strategically substituted nitrogen containing (aza-) and sulfur containing (thio-) pentalene ligand-metal complexes produce active catalysts which make polypropylene having high melting point and high molecular weight.[4] In this case, changing the heteroatom affected the electron donation of the ligand to the metal center. We have reported distinct, favorable response in moving from nitrogen containing heterocenes to more electropositive sulfur containing heterocenes, both in catalyst activity and polymer properties.[5,6]

One of the first zirconium-containing heterocenes synthesized uses 5-methylcyclopenta[b]thiophene (Scheme 1) as a ligand. The methods used for preparation and bridging were modified from the literature.[7] Changing the sulfur-containing heterocene complex to contain a selenium atom was performed following similar methods.



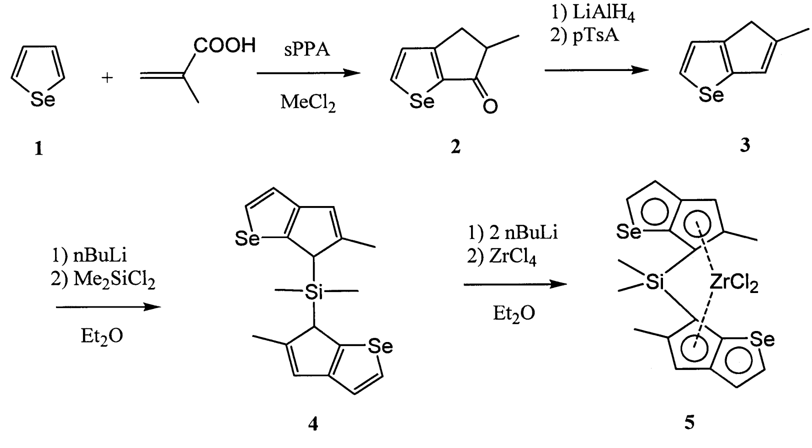
SCHEME 1

Sulfur-containing ligands having geometry similar to 2-methyl-1*H*-cyclopenta[a]napthalene were synthesized using synthetic strategies similar to those developed for thiophene.[3] We chose methods for tellurium that would allow us to use readily-available starting materials and chemistry that we have developed for heterocenes containing sulfur.

Our goal was to explore the potential of the selenium and tellurium chalcogens in heterocene ligands with the possibility of affecting the electronics at the metal center as well as the size and composition of the ligand field during olefin polymerization. The application of synthetic strategies that were available from sulfur-containing heterocene ligands were applied and are discussed. This report summarizes the work done on the synthesis and characterization of the previously unreported selenium-containing complex dimethylsilanebis(η^5-5-methylcyclopenta[*b*]selenophen-yl)zirconium dichloride (**5**) and bis(η^{5-}3-methylcyclopenta[b][1]benzotelluraphen-yl)zirconium dichloride (**9**). In addition, polymerizations with propylene or ethylene were carried out to provide comparative data for use in evaluating and designing other heterocenes.

RESULTS

Methods for cobbling a cyclopentadiene (Cp) ring onto either selenophene (**1**) or benzo[*b*]tellurophene (**6**) were carried out as previously reported for thiophene or benzo[*b*]thiophene and are shown in Scheme 2.[1,2] The initial reaction involved adding a solution of either **1** or **6** and methylacrylic acid in dichloroethane to super polyphosphoric acid (sPPA).[5,6,8] This reaction is not regiospecific and two ketone isomers are produced in a ~2:1 mixture in the reaction which are apparent from gas-chromatography/electron impact mass spectrum (GC-EIMS) and ^{1}H-NMR analysis for either complex. This situation was well described by Ryabov et al. for the thiophene series.[9]



$Me_2Si(5\text{-methyl-selenopentalene})_2ZrCl_2$

SCHEME 2

After initial formation of the ketone isomers (for example: 5-methyl-4,5-dihydro-4*H*-cyclopenta[*b*]selene-6-one (**2**), conversion to alcohol by treatment with lithium aluminum hydride in diethyl ether was followed by treatment with *para*-toluenesulfonic acid monohydrate in refluxing toluene to form the olefin (**3**) in an overall yield of 46%. Bridging of (**3**) was done by treatment with n-butyllithium, followed by addition of this reaction mixture to a cold concentrated tetrahydrofuran (THF) solution containing dichlorodimethylsilane. After warming to ambient temperature, stirring overnight, and water work-up, the complex (**4**) was isolated as a red powder in 44% yield. The ligand was deprotonated in ether and zirconium tetrachloride was added as a dry powder. The complex **5** was isolated by filtration to remove LiCl, and drying.

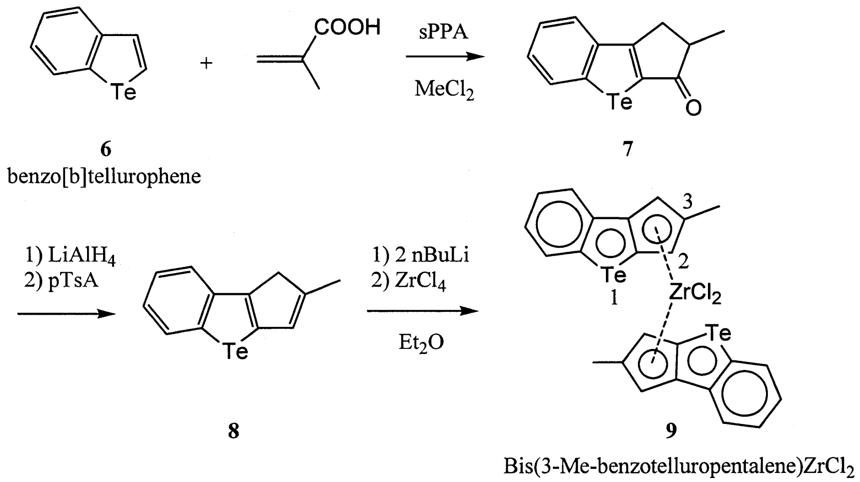
Intermediates towards the synthesis of (**5**) were characterized by ^{1}H-NMR and GC-EIMS. In the EIMS, typical isotope abundance profiles for selenium containing complexes are found in each of the intermediates analyzed and are underscored in the experimental section. The final complex was isolated with difficulty after washing with pentane and filtering with diethyl ether. The final complex had low stability (indicated by formation of black solids during isolation steps) and was filtered from a toluene solution prior to polymerization testing.

Yields for the construction of the Cp-ketone varied depending on the chalcogen. Results from the synthesis showed 2 isomers were formed in a 2:1 ratio. The predominate isomer is presumed to form by the initial reaction of the methacrylic acid cation at the carbon α- to the chalcogen atom (the 2-position of the chalcophene ring). The isomeric ketone is formed by the attack at the β-carbon (position 3 on the chalcophene ring). The ratio of the isomers and the factors that control isomeric formation was similar for either of the chalcogens ligand systems studied.

We previously have reported the use of 3-methylbenzothiopentalene in ligands for producing elastomeric polypropylenes.[10] Starting with commercially available benzo[*b*]thiophene (thianapthalene) and adding a five-membered cyclopentadiene ring via the Nazarov cyclization (described above), we effected the synthesis of a cyclopentabenzothiopentylene-ketone which was converted to the desired olefin. Methods for the preparation of the tellurium-containing 3-methylbenzotelluropentalene analog followed this same procedure (Scheme 3).

Benzo[*b*]tellurophene was either prepared following literature procedures,[11] or purchased commercially. After treatment with methacrylic acid in the presence of sPPA, a mixture of 2-methyl-2,3-dihydro-1*H*-cyclopenta[b]benzotellurophen-1-one **7a** and 2-methyl-1,2-dihydro-3*H*-cyclopenta[b]benzotellurophen-3-one **7b** were identified by gas chromatography/ion impact mass spectrometry (GC-EIMS) and ^{1}H-NMR. The synthetic steps for conversion of the ketone **7** to the alcohol, dehydration to the olefin **8** followed methods described for the selenophene containing ligand prepared above. Deprotonation of the olefin and addition to zirconium tetrachloride to produced the zirconocene pre-catalytic complex as identified by ^{1}H-NMR.

The ^{1}H-NMR from the synthesis of the tellurium containing complex of (**9**) is included in Figure 1. The spectra at the bottom of the figure is the starting olefin for the complex, the upper spectra are from the zirconium containing complexes and an expansion of the aromatic region from the same spectra. For the starting benzotellurapentalene olefin (**8**), the characteristic doublet-doublet triplet-triplet pattern for



SCHEME 3

the aromatic region is found for the aromatic region between 7.0 ppm and 8.0 ppm. The olefinic proton on the Cp ring is found at 6.6 ppm, and the aliphatic Cp protons are found at 3.35 ppm. The signal for the methyl group on the Cp ring is shifted further up field at 2.2 ppm.

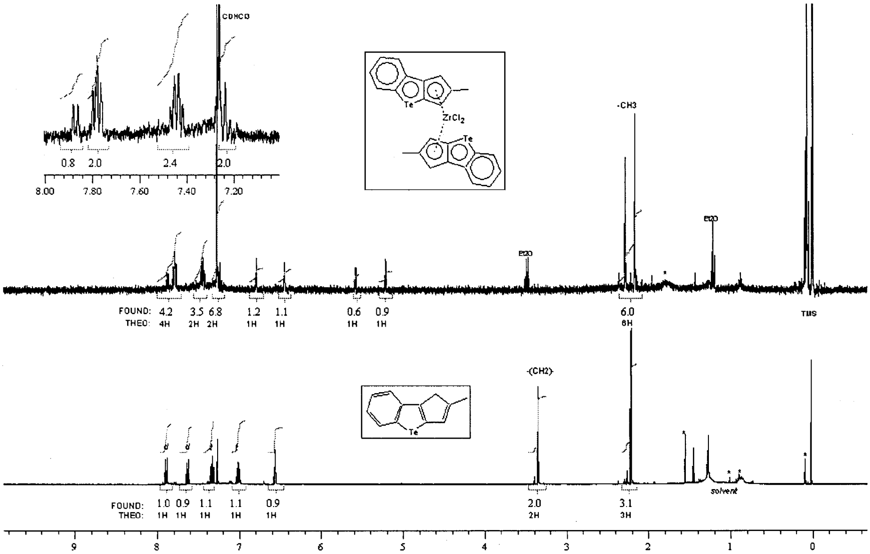


FIGURE 1 ^{1}H-NMR of complex **8** and **9**.

The isomers from the synthesis of the **9** are from the tellurium atom in the molecule located on the same side or different sides of the complex. The four signals found between 5.2–6.8 ppm arise from the 4 different environments found for the Cp ring protons from isomers formed in the synthesis. The expansion of the region between 7–8 ppm is complicated by the overlapping signals from the protons on the aromatic ring. Two isomers are also distinguished as two methyl signals found around 2.2 ppm.

EIMS analysis of the product from the reaction of the anion prepared from **8** with $ZrCl_4$ is seen in Figure 2. The analysis of the fragmentation pattern from the mass of the zirconocene all show a characteristic-natural-isotope abundance pattern for double-tellurium-containing complexes. The parent ions centered at 724 emu ($M2^+$) are followed by loss of 126 (M2-Zr-HCl) at 598 emu, and 162 (M2-Zr-2HCl) at 562 emu. Additional fragments centered at 443 emu (loss of 281; $[M2 - \mathbf{8}^+]$), and at 284 emu ($\mathbf{8}^+$) are followed by loss of the tellurium atom from olefin found centered at 154 emu.

Polymerization Results

Complexes **5** and **9** produced in the synthetic scheme described above were used as is: no separation of isomers or attempts to isolate rac

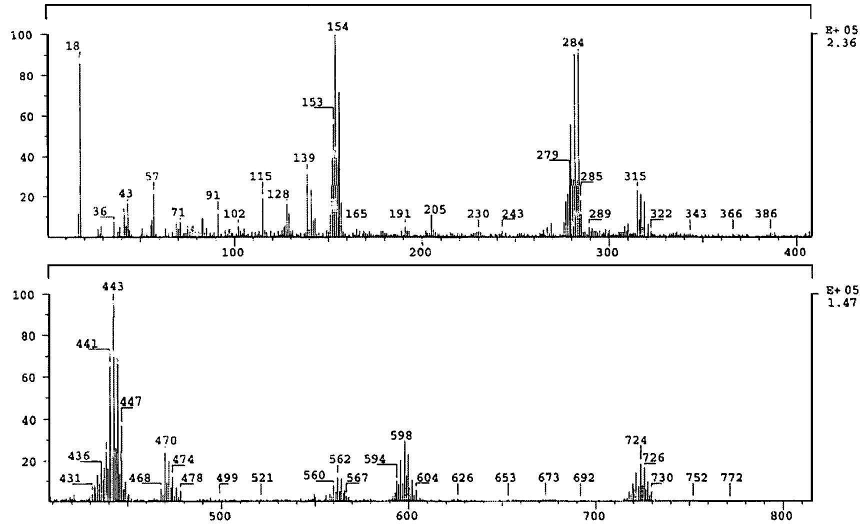


FIGURE 2 Electron ionization mass spectrum of Bis(3-Me-benzotelluropentalene)$ZrCl_2$ (**9**).

TABLE I Propylene Polymerization Results Using 5 [Me_2Si(5-methyl-selenopentalene)$_2ZrCl_2$]. Polymerization Conditions: 1L autoclave (bulk propylene), 20 mg catalyst, 10 mL 10% MAO solution, Al/Zr = 420, 1 h

run	H_2 (mmol)	Polymn temp °C	Polymer yield (g)	Productivity Kg PP/g cat/h	Tm2 °C	I.V. (dL/g)	GPC Mw 10^{-3}	GPC Mw/Mn	XS RT (%)
1	0	50	19	1.0	140	1.2	183	6.5	47
2	100	50	28	1.4	143	0.7	92	5.1	38
3	0	70	43	2.2	135	0.8	102	2.8	27
4	100	70	56	2.8	138	0.4	49	3.3	30

or meso isomers was followed. Either complex was activated with methyl aluminoxane (MAO) then tested in ethylene or propylene polymerizations.

Results from propylene polymerizations with **5** at 50°C and 70°C with and without hydrogen are included in Table I. Polymerizations at lower temperature (50°C) produced polymer having higher molecular weight than polymer made at 70°C. Increasing hydrogen concentration increased catalyst productivity while decreasing polymer molecular weight.

Productivity of **5** is indicated in Table I as Kg PP/g cat/h: the broad molecular weight distributions (M_w/M_n) which were higher at lower temperatures could be due to differences in *-rac* or *-meso* activities at the different temperatures tested or to greater catalyst decomposition leading to alternative catalytic species. At 70°C with no added hydrogen however, the polymer had a melting point of 135°C and a distribution of 2.8. This polymer result lies between that found with the sulfur analog (under identical conditions produces a polymer having a melting point of 125°C) and the carbon-containing analog Me_2Si(2-MeInd)$_2ZrCl_2$ (polymer melting point 145°C under identical conditions). This indicates that the development of alternative complexes having greater stability may produce (more) active highly stereoregular catalysts.

The xylene insoluble fraction from the polymer made at 70°C with no hydrogen (entry 3) was fractionated (xylene insolubles) and the polymer analyzed by ^{13}C-NMR. The xylene insoluble fraction had mmmm of 83.32% and mrrm of 2.66% (see Table II).

The ^{13}C-NMR data is in agreement with the melting point of the "as polymerized" data for this polymer and further shows that the complex makes isospecific polypropylene following the enantiomorphic site control model.[10,12] The catalyst had fairly high regioselectivity (0.33 mol%)

TABLE II ^{13}C-NMR Analysis; Xylene Insoluble Fraction of Polymer Made With 5 [$Me_2Si(5\text{-}Me\text{-}selenopentalene)_2ZrCl_2$] vs 11 [$Me_2Si(5\text{-}Me\text{-}thiopentalene)_2ZrCl_2$] at 70°C[a]

Pentad	Complex **5**[b] (selenium)	Complex **10**[b] (sulfur)
mmmm	82.54	71.62
mmmr	6.14	10.14
rmmr	0.44	2.21
mmrr	5.45	7.27
mrmm + rmrr	1.48	2.06
mrmr	0.44	1.42
rrrr	0.40	0.86
rrrm	0.64	0.88
mrrm	2.47	3.54
Single unit errors per 1000 propylene units	28.02	41.35
Polymer Tm2[c]	135°C	125°C
I.V. (dL/g, decalin)	0.80	0.98
Mw (GPC)	102	273
Mw/Mn	2.8	2.6
XSRT	27	33

[a] See text for polymerization conditions.
[b] Xylene-insoluble fraction.
[c] Temperature rising elution fractionation (TREF), 100°C fraction.

2,1 (E) type errors, typical for metallocene catalysts with C_2-symmetry and methyl substituents α- to the bridgehead carbon.

For the tellurium containing complex **9**, polymerization results are included in Tables III and IV. Three polymerizations with ethylene were done at varying Al/Zr ratios. The lower Al/Zr ratio polymerization had lower activity but gave higher molecular weight polymer, probably due to reduced transfer to aluminum as a chain termination mechanism.

TABLE III Ethylene Polymerization Results at Varying Temperatures Using 9 [Bis(3-Methyl-benzotelluropentalene)$ZrCl_2$]. Polymerization Conditions: 1L Autoclave, 600 mL Hexane (Solvent), Ethylene Added to 6.8 Bar (100 psig)

Polym. temp. °C/time (h)	Catalyst (mg)	Al/Zr (mol)	Yield (g)	Productivity (g pol./g cat./h)	M_W(GPC)	M_W/M_n
50°C (1 h)	5.0	226	16.5	3,300	—	—
70°C (2 h)	5.3	433	42.2	3980	81,000	4.4
80°C (1 h)	0.5	4580	12.0	24000	51,500	1.8

TABLE IV Comparative Polymerization Results[a] with (12) [Bis-(3-methyl-benzothiopentalene)ZrCl$_2$] and (9) [Bis-(3-Me-benzotelluropentalene)ZrCl$_2$]

Catalyst/ monomer	Cat. (mg)	Time (min.)	Polymn temp °C	Yield (g pol)	Productivity (g pol./g cat./h)	IV (dL/g)	Tm (°C)	Hc (J/g)
12 PE	0.1	30	80	24	476000	3.6	141	196
12 PE	0.1	30	40	10	168000	9.2	144	164
12 PE	0.1	30	20	139	140000	9.7	144	142
12 PE	0.1	30	0	6	55000	10.3	146	153
9 PE	0.1	60	80	1	24000	2.7	139	124
9 PE	0.2	60	40	4	20500	8.5	142	191
9 PE	0.2	30	20	3	14500	6.8	146	12
9 PE	0.2	30	0	1	5000	5.2	139	16
12 PP[b]	1.0	30	70	25	50800	0.14	—	—
9 PP[b]	5.0	30	70	8	3160	0.16	—	—

Polymerization conditions:

[a] 1L autoclave, 600 mL heptane, 10 bar ethylene, 2 mmol TiBAl, Al/Zr = 5100.

[b] Bulk propylene.

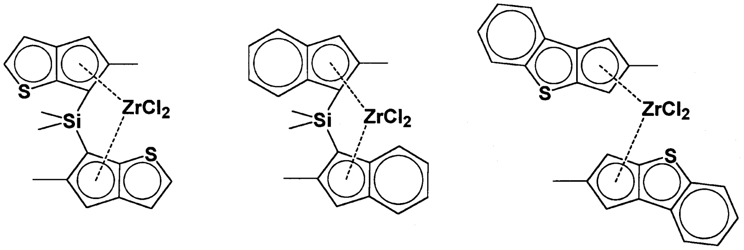
At 70°C, in a 3.78 l reactor using 1 mg of catalyst and 10 mL MAO, this catalyst made 5 g of polymer in 1 h. This result is a productivity of 5000 g PP/g cat./h. The propylene polymer prepared in this fashion had a sticky consistency, typical of a low molecular weight atactic material (M_w = 12300). The polymer molecular weight distribution was wider than expected for a single site catalyst, indicating that some decomposition to alternative active species was probable.

Ethylene polymerizations with **9** (Bis-2-methylbenzotellurophene zirconium dichloride) (Table III) were carried out in a 600-mL reactor using 400 mL of hexane as a solvent. The catalyst was reacted with MAO for 15 min., then transferred to the reactor via cannula/nitrogen pressure. After the reactor had reached the desired temperature, ethylene gas was added to the pressure indicated in Table III.

Conditions under which the catalyst was run greatly effects polymerization result. At higher Al/Zr ratios, the catalyst became much more active. Higher temperature polymerizations made polymer with lower molecular weight. The polymer dispersity (M_w/M_n) decreased from 4.4 (indicating decomposition) to 1.8 (indicating stability).

The tellurophene catalyst was less active than the sulfur-containing catalyst, although the varying catalyst concentration greatly affected the activity indicating that polymerization conditions could be further optimized.

Comparative polymerizations with the sulfur-containing bis(benzo-[b]thiopentalene)zirconium dichloride (**10**) are included. Productivity



10 **11** **12**

$Me_2Si(5\text{-}Me\text{-}thiopentalene)_2ZrCl_2$ Bis(3-Me-benzothiopentalene)$ZrCl_2$

SCHEME 4

of **9** towards ethylene was lower than the sulfur analog **10** and polymer molecular weights were lower at the same temperature. Both the sulfur and the tellurium complex made amorphous polypropylene polymer. The tellurium-containing catalyst also had lower activity towards propylene, but produced similar molecular weight.

DISCUSSION

Two chalcogen-containing heterocene complexes were made and characterized and both were active in olefin polymerizations.

The complex-containing selenium atoms were fashioned into an isotactic ligand framework and produced isotactic polymer. The Se-containing complex had low stability under the conditions of the synthesis and questionable stability under the polymerization conditions. The polymer melting point and crystallinity fall between that of the sulfur analog and the carbon analog for this catalyst system. The selenium atom (in selenophene) has larger α-carbon bond distances than sulfur and may provide additional torsions in the ligand field (steric influences) more over than electronics.[11]

Catalyst made from the unbridged 3-methylbenzo-telluropentalene produced amorphous polypropylene (as predicted), with low molecular weight. The polyethylene made from this complex has high molecular weight, but the catalyst complex has lower activity than the sulfur analog. Catalyst activity increased with increasing MAO concentrations in the polymerization mixture with a concurrent increase in molecular weight.

Additional stability built into these ligand system by adding methyl substitutions at the 2 position in the selenapentalene/zirconocene complex and bridging the benzo-telluropentalene ligand with, silicon are future synthetic steps in the process of producing stable, bridged, highly active, isospecific, chalcogen-containing zirconocenes.

EXPERIMENTAL: GENERAL PROCEDURES

All manipulations with air-sensitive materials were performed under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmosphere drybox (except polymerizations, which were conducted using argon as the inert gas). Anhydrous solvents were obtained from Aldrich and used without further treatment. Mass spectra of the ligand was measured with a Hewlett Packard 6890 series gas chromatograph equipped with a 5973 mass-selective detector (EI, 79 eV). Mass spectra of the zirconocenes were measured using a direct insertion probe (DIP) in either chemical ionization or electron ionization mode.

EXPERIMENTAL: PREPARATION OF THE COMPLEXES

5-Me-5,6-dihydrocyclopenta[*b*]selenophen-4-one 2

A solution of selenophene (9.9 g, 75.6 mmol) and methacrylic acid (7.8 g, 90 mmol) in 50 mL of dichloroethane was added dropwise to 250 g of super PPA at 80°C and stirred for 1.5 h. The mixture was poured onto crushed ice and stirred until the PPA was completely decomposed. The product was extracted with 30% (v/v) dichloromethane in hexane. The combined organic fractions were washed with a saturated aqueous solution of $NaHCO_3$ and dried ($MgSO_4$). Solvents were removed on a roto-evaporator leaving 5.25 g of crude product that was 35% product by GC analysis. The crude product was chromatographed on silica using dichloromethane and gave 3.02 g of the target. Yield: 35%. ^{1}H-NMR (CD_2Cl_2): 8.6 (d, 1H), 7.25 (d, 1H), 3.25 (dd, 1H), 2.9 (m, 1H), 2.58 (dd, 1H), 1.3 (d, 3H); ^{13}C 201.8, 169.5, 145.5, 144.7, 143.3, 126.3, 45.9, 34.4, 16.8; MS (EI, 70 eV): $[M]^+$ *m/z (%)*; 200 (88), 185 (100), 171 (13), 157 (22), 145 (7), 130 (9), 120 (11) 91 (55).

5-Me-5,6-dihydrocyclopenta[1,2-b]selenophen-4-ol 2b

In a 250 mL flask was placed 20 g (100 mmol) **2** dissolved in 60 mL diethyl ether. Dropwise, a solution containing lithium aluminum hydride (1.0 M in diethyl ether, 100 mmol, 100 mL) was added at −78°C. After addition was complete, the temperature was allowed to warm to ambient, then stirred an additional 3 h. Water was then slowly added (50 mL) and the organics were filtered through Celite, collected with diethyl ether, washed with water, then dried (with magnesium sulfate).

The solvents were removed in vacuo: 12.9 g dark red oil: two isomers: 98.6% by GCMS (major isomer, 63%); MS (EI, 70 eV): *m/z* (%); 205 (2), 204 (19), 203 (14), 202 (100), 201 (21), 200 (51), 199 (26), 198 (22), 187 (51), 186 (8), 185 (40), 184 (29), 183 (41), 182 (17), 181 (19), 180 (10), 175 (5), 174 (9), 173 (24), 172 (6), 171 (16), 170 (9), 169 (15).

5-Methyl-3-hydrocyclopenta[*b*]selenophene 3

In a 500-mL flask 5-Me-5,6-dihydrocyclopenta[*b*]selenophen-4-ol **2b** (13.0 g, 65 m mol) was dissolved in 70 mL toluene and 0.2 g para-toluene sulfonic acid monohydrate was added. The flask contents were stirred at room temperature for 18 h, then the reaction mixture was washed with water, the organics were collected with diethyl ether, dried over magnesium sulfate, filtered, then solvents were removed in vacuo. 12.3 g of dark red oil was collected. 11 g were chromatographed with hexane through silica: 0.6 g of a light yellow oil were collected from selective fractions: 90% by GC (major isomer, 59%). MS (EI, 70 eV): $[M]^+$ *m/z* (%); 186 (2), 185.9 (18), 184.8 (25), 183.9 (100), 182.9 (92), 181.9 (92), 181.9 (60), 180.9 (63), 179.9 (45), 178.9 (23), 168.8 (27), 166.9 (13).

Bis-(5-methyl-6H-cyclopenta[b]selenophen-6-yl)-(dimethyl)silane 4

In a 200-mL flask containing 0.6 g (3.2 mmol) **3** dissolved in 40 mL diethyl ether was added a solution of n-butyllithium (2.5 M in hexane, 3.2 mmol, 1.3 mL) at room temperature dropwise. The flask contents were stirred for 1 h. A small amount of THF was added to dissolve the solids and facilitate the reaction.

In a separate 250-mL flask with 125-mL addition funnel was added 0.21 g (1.6 mmol) dichlorodimethylsilane dissolved in 40 mL THF. The solution was cooled to −78°C, and the solution containing the dianion prepared above was added dropwise. The flask contents were allowed to warm to room temperature then stirred for 18 h. The reaction mixture was quenched with 40 mL of a saturated solution of ammonium chloride (added dropwise). The organics from the reaction mixture were collected with diethyl ether, washed with water, dried over magnesium sulfate, filtered, then the solvents were removed in vacuo. 0.56 g dark orange oil was collected and chromatographed on silica using hexane as the eluent. 0.3 g product (50% by GCMS); MS (EI, 70 eV): $[M]^+$ *m/z* (%); 426.9 (1), 425.8 (4), 424.8 (2), 423.8 (10), 422.8 (3), 421.8 (9), 242.9 (13), 241.9 (12), 240.9 (59), 239.9 (12), 238.9 (31), 237.9 (15), 236.9 (13), 160 (20), 159 (100), 157 (2).

Dimethylsilanediylbis(η^5-cyclopenta[b]selenophen-6-yl) Zirconium Dichloride 5

A 100-mL flask was placed 0.3 g (0.71 mmol) **4** and dissolved in diethyl ether. Dropwise, a solution containing n-butyllithium was added (3 mmol, 1.2 mL, 2.5 M in hexane). The reaction mixture was stirred for 20 min. The solvents were removed in vacuo. The solids were washed with pentane, then re-slurried in fresh pentane. 0.2 g (0.8 mmol) zirconium tetrachloride was added slowly to the stirred slurry as a dry powder. The reaction mixture was stirred over night, then filtered, and the solids collected were washed with pentane. The solids were dissolved in diethyl ether, filtered, then the solvents removed in vacuo. 0.48 g was collected and used in subsequent polymerization studies. ^{1}H-NMR (CD_2Cl_2): 7.0–7.4 (m, 6H), 2.38 (s, 6H), 0.5 (s, 6H).

Mixture of 2-Methyl-2,3-dihydro-1*H*-cyclopenta[b]-benzotellurophen-1-one 7a and 2-Methyl-1,2-dihydro-3*H*-cyclopenta[b]benzotellurophen-3-one 7b

In a 100-mL flask with reflux condenser and mechanical stir, containing 90 g super polyphosphoric acid (sPPA) was added a solution containing 92 g (40 mmol) benzo[b]tellurophene, and 3.4 g (40 mmol) methacrylic acid dissolved in 10 mL dichloroethane. The reaction mixture was stirred at 100°C for 3.5 h, then poured onto ice. After the PPA had decomposed, the organic fraction was collected with a 20% dichloromethane/hexane (v/v) solution, The organic fraction collected in this manner was washed with water, a saturated solution of sodium bicarbonate, then water. The organic fraction was dried over magnesium sulfate, filtered, then the solvents were removed in vacuo. 2.47 g of dark red oil was recovered. Yield: 20.5%. ^{1}H-NMR (δ, ppm, $CDHCl_2$, 2 isomers): 7.0–8.05 (m, 4H), 3.5 (m, 1H), 2.95 (m, 1H), 2.8 (2d, 1H), 1.3 (2s, 3H); EIMS: m/z (%) 302 (1), 301 (13), 300 (100), 299 (17), 298 (94), 297 (12) 296 (60), 295 (26), 294 (16), 293 (4), 285 (8), 283 (7), 283 (60), 282 (5), 281 (38), 279 (15), 279 (10).

2-Methyl-3*H*-cyclopenta[*b*]benzotellurophen-1-ol 7b

In a 100-mL flask with pressure equalized addition funnel, sidearm and stirring bar was added 2.47 g (8.3 mmol) 2-Methyl-2,3-dihydrobenzo[b]cyclopenta[d]tellurophen-1-one dissolved in 20 mL diethyl ether. Dropwise, at room temperature, a solution containing lithium aluminum hydride (5 mmol, 5 mL, 1M in diethyl ether) was added. The reaction mixture was stirred for 18 h, then slowly quenched with

3 mL of a saturated solution of ammonium chloride. The organics were collected for the reaction mixtures with diethyl ether, washed with water, dried over magnesium sulfate, filtered, then solvents were removed in vacuo. 2.47 g orange oil were recovered. Yield: 98.5%. FID GC and GCMS indicate 2 isomers (68% and 31%) both having identical mass: EIMS: *m/z* (%) (major isomer): 303 (13), 302 (100), 301 (19), 300 (95), 299 (14) 298 (59), 297 (26), 296 (16), 295 (5), 294 (8), 285 (14), 284 (41), 283 (17), 282 (43), 281 (11), 280 (28), 278 (13), 279 (13), 278 (9), 273 (10), 269 (13), 259 (13), 257 (12); ^{1}H-NMR (δ, ppm, $CDHCl_2$, both isomers): 7.0–8.0 (ddtt, 4H), 4.8–5.2 (2d, 1H), 2.4–3.5 (m, 4H), 1.3 (m, 3H); ^{13}C-NMR (δ, ppm, $CDHCl_2$) (both isomers): 133.3, 126.6, 126.3, 125.7, 125.1, 124.9, 86.5, 79.9, 46.7, 40.8, 38.0, 37.4, 19.3, 14.9.

2-Methyl-3*H*-cyclopenta[*b*]benzotellurophene 8

2.45 g (8.11 mmol) 2-Methyl-3H-benzo[b]cyclopenta[d]tellurophen-1-ol was dissolved in 40 mL toluene and 0.05 g para-toluenesulfonic acid monohydrate was added. The reaction mixture was refluxed for 1 h. The organics were collected with diethyl ether, washed with water, dried over magnesium sulfate, filtered, then the solvents were removed in vacuo: 1.62 g dark red oil. Yield: 68.2%. MS (EI, 70 eV): $[M]^+$ *m/z* (%); (major isomer): 285.9 (1), 285.0 (9), 283.9 (75), 283.0 (16), 281.9 (77), 280.9 (12), 279.9 (50), 278.9 (20), 277.9 (17), 276.9 (5), 275.9 (7), 274.9 (1), 268.9 (10), 267.9 (1), 266.9 (10), 265.9 (1), 264.9 (6), 263.9 (2), 155.1 (14), 154.1 (100), 153.1 (72), 152 (54), 151 (19), 150 (8). ^{1}H-NMR (□, ppm, $CDHCl_2$): 7.0–8.0 (ddtt, 4H), 6.58 (s, 1H), 3.3 (2s, 2H), 2.2 (2s, 3H); ^{13}C-NMR (δ, ppm, $CDHCl_2$); 150.4, 146.5, 142.3, 134.6, 133.9, 133.3, 129.1, 125.9, 124.8, 124.3, 124.2, 123.1, 43.0, 16.9, 16.8.

Bis(η^5-2-methyl-cyclopenta[b]benzotelluraphen-yl)zirconium Dichloride 9

A 250-mL round bottom flask was placed 0.7 g (3.7 mmol) 2-methyl-4,5-benzothiopentalene dissolved in 10 mL diethyl ether. Dropwise, 1.5 mL (3.75 mmol) of a 2.5 M solution of n-butyllithium in hexane was added at room temperature. Stirring was continued for 1 h. The solvents were removed in vacuo. The light brown powder that was isolated was washed with pentane, then 0.43 g (1.85 mmol) zirconium tetrachloride was added. The mixture was then slurried with pentane (30 mL), and a small amount of diethyl ether (2 mL). The mixture turned bright yellow; stirring was continued 18 h. Solvents were then removed in vacuo leaving 0.66 g of a light brown powder. A small amount of this material was slurried in toluene, filtered, then the toluene was slowly evaporated to produce crystals that were suitable for X-ray crystallography studies. Yield was 90%. ^{1}H-NMR (δ, ppm, CD_2Cl_2): 8.0 (4H), 7.3–7.5 (4H), 6.5 (s, 1H), 6.3 (s, 1H), 5.9 (s, 1H), 5.5 (s, 1H), 2.0–2.1 (2s, 6H). ^{13}C-NMR (CD_2Cl_2): δ 127.0, 126.9, 125.5, 125.4, 123.9, 123.8, 123.6, 123.5, 107.9, 106.4, 106.1, 105.2, 66.8, 17.3, 17.1, 14.5.

Bis(η^5-2-methyl-cyclopenta[*b*]tellurophen-yl)zirconium Dichloride 9

A 200-mL flask was placed 1.6 g (5.6 mmol) 2-Methyl-3H-benzo-[b]cyclopenta[d]tellurophene dissolved in 40 mL diethyl ether. Dropwise, a solution containing n-butyllithium (5.6 mol, 2.5M in hexane, 2.3 mL) was added at room temperature. Stirring was continued for 2 h. Then the solvents were remove in vacuo and the solids were washed with pentane. To the pale yellow solids was added 0.53 g (2.3 mmol) zirconium tetrachloride and the mixture was slurried in fresh pentane. A small amount of diethyl ether (1 mL) was added and the reaction mixture was stirred for 18 h. Solvents were then removed in vacuo: 1.85 g yellow/orange powder. 1.01 g were filtered from dichloromethane and the solvents removed in vacuo: 780 mg dark red powder was recovered: Yield: (~36%). For NMR analysis, the solids were filtered from $CDHCl_2$: ^{1}H-NMR (ppm, $CDHCl_2$)(both isomers): 7.0–8.0 (ddtt, 4 H), 6.7 (s, 1H) 6.45 (s, 1H), 5.65 (s, 1H), 5.35 (s, 1H), 2.2 (s, 3H), 2.05 (s, 3H).

Polymerizations Using 9

Initial polymerization with ethylene reported in Table III were carried out in a 600-mL reactor using 400 mL of hexane as a solvent. The catalyst was reacted with MAO for 15 min, then transferred to the reactor via cannula/nitrogen pressure. After raising the reactor temperature to the temperature indicated in Table III, ethylene was added. The polymerization was complete, the reactor was vented and the reactor contents quenched with methanol. After purging with nitrogen, the polymer was collected, dried in vacuo, weighed, then a portion submitted for analysis.

Ethylene Heptane Slurry Polymerizations

Polymerizations were conducted in a 1 L stainless steel autoclave equipped with a mechanical stirrer and oil thermostat temperature controlled jacket. The autoclave was swept with dry nitrogen at 90°C for 1 h prior to polymerization. After cooling the reactor to 30°C, solvent (500-mL heptane purified over 3 Å molecular sieves) and 2 mL TiBAl (scavenger) was added to the reactor. The metallocene compound was dissolved in toluene to a desired amount, then 1 mL of this solution was added to the calculated amount of MAO solution (to obtain an Al/Zr molar ratio indicated in Tables III and IV), and the color change recorded. The catalyst/MAO mixture was agitated for 10 min, then added to the reactor via syringe. The stirrer was set at 300 rpm, the reactor temperature was raised to 80°C, and then ethylene overpressure was added. Constant overpressure was maintained throughout the run. In all polymerization tests, the stirring was stopped, the reactor vented while cooling to room temperature. The reactor was purged with nitrogen to remove residual monomer, 5 mL methyl alcohol was added to quench the contents. The polymer was removed, filtered, and dried in a vacuum oven at 50°C for 4 h before weighing. Reported activities were calculated from dried polymer weight.

Bulk Propylene Polymerizations

In a 1 L stainless steel thermostated reaction vessel (Buchi) was added a solution containing triisobutyl aluminum (4 mmol, 4 mL, 1M solution in toluene). At 30°C, 250 g propylene was added and the temperature of the reactor contents brought to 50°C. A solution containing the catalyst and activator (10% MAO in toluene) was added though an addition tube using 50 g propylene. The reactor was brought to reaction temperature and stirred at constant temperature for the time listed in the data Table IV. The reaction stirring was stopped, the propylene was vented and the temp was reduced to 30°C. Methanol was added to quench the reactor contents and the system was purged with nitrogen. The reactor was opened and the polymer contents were collected. Polymers were dried in vacuo at 60°C for 6 h, then sent for analysis.

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