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## Introduction

The polyolefin industry continues to grow steadily because of continuous discoveries of new catalysts, processes, and polyolefin materials with new properties. While early transition metal catalysts generally have high activity for olefin polymerization, their oxophilicity has largely prevented their use for incorporation of polar olefins.1 During the last two decades, significant advances have been made in the development of late-transition-metal polymerization catalysts. A few notable examples include the Ni( $\pi$ )- and Pd( $\pi$ )- $\alpha$ -diimine systems discovered by Brookhart and coworkers<sup>2</sup> and the Pd(II)-orthophosphino-arenesulfonate system initially introduced by Drent and coworkers.3 Excitingly, some of the late transition metal catalysts are able to copolymerize functional olefins such as methyl acrylate (MA).<sup>2a,3,4</sup> Following these pioneering studies, a number of groups have made important contributions to this area both in new catalyst design and new polymer synthesis.<sup>5</sup> Despite their promising attributes, late transition metal catalysts are generally less active than early transition metal catalysts, warranting the search for other transition metal complexes for olefin polymerization.

An ideal catalyst system should combine the functional group tolerance of late transition metals with the high activities of early transition metals. Group 8 metals, located right in the center of the transition metal block in the periodic table, may

# Direct observation of a cationic ruthenium complex for ethylene insertion polymerization<sup>†</sup>

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We report here the first direct observation of a cationic ruthenium complex catalyzing ethylene insertion polymerization. An arene-tethered ruthenium complex ( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>SCH<sub>3</sub>RuCl<sub>2</sub>) (**3**) was synthesized and shown to be able to catalyze ethylene polymerization upon activation with AlMe<sub>2</sub>Cl. For mechanistic studies, we synthesized the homologous dimethylated  $\eta^6$ -C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>SCH<sub>3</sub>Ru(CH<sub>3</sub>)<sub>2</sub> (**4**) complex, which upon activation with the Brookhart acid ([H(Et<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> [BAr'<sub>4</sub>]<sup>-</sup>) was also active for ethylene insertion polymerization. <sup>1</sup>H-NMR and mass spectrometry (MS) studies provide direct evidence for a ruthenium cationic [ $\eta^6$ -C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>3</sub>SCH<sub>3</sub>Ru(oligomer)]<sup>+</sup> complex as the active species during polymerization. This has unambiguously shown for the first time a ruthenium complex as the active species for catalyzing olefin insertion polymerization.

offer the possibility of combining such good attributes. In particular, ruthenium complexes have proven to be very versatile in various types of catalytic reactions and show excellent functional group tolerance.6 Although best known for metathesis polymerization,<sup>6c</sup> ruthenium has also been sporadically investigated for olefin insertion polymerization.7 In early 1970's, hydrido-ruthenium species - HRuCl(PPh<sub>3</sub>)<sub>3</sub> or (H)<sub>2</sub>Ru(PPh<sub>3</sub>)<sub>4</sub> were reported for insertion polymerization of ethylene or polar olefins.<sup>7a,b</sup> Later, Nomura et al.<sup>7c,d</sup> reported a ruthenium-pybox complex (1) (Chart 1), which in combination with MAO could polymerize ethylene. However, in a detailed study by Brookhart and coworkers,<sup>7e</sup> a similar Ru-diiminopyridine complex (2) was shown to be completely inactive despite the fact that analogous Fe(II)-diiminopyridine complexes showed excellent activity toward ethylene insertion polymerization.8 The authors attributed the inactivity to the coordination geometry of the Ru complex. The distorted square pyramidal coordination of Ru complex 2 results in non-degenerate coordination sites of olefin and alkyl groups relative to the tridentate ligand, resulting in a prohibitively high energetic barrier for migratory insertion. Indeed, a recent computational study calculated that the



**Chart 1** Reported complexes **1** and **2**, and our complex **3**. Both **1** and **2** have non-equivalent coordination sites for the putative olefin and alkyl groups of the active growing species. The designed complex **3** has two equivalent *cis* coordination sites.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures, synthesis, and characterization of compounds. Detailed <sup>1</sup>H-NMR and ESI-MS studies on active polymerization species. Polymerization studies and X-ray structures. See DOI: 10.1039/c3sc50676b

barriers for migratory insertion of the coordinated olefin into the Ru alkyl bond in 1 and 2 are larger than 25 kcal mol<sup>-1</sup>, too high for olefin insertion polymerization.<sup>9</sup> Very recently, Claverie *et al.* reported a Ru–di(phosphine-arenesulfonato) complex that surprisingly made *crosslinked* polyethylene.<sup>10</sup> *Notably, none of the aforementioned studies have elucidated the active species responsible for olefin insertion polymerization.* 

On the basis of these previous studies, we hypothesized that it would be possible to achieve active Ru(n) complexes for insertion polymerization if they are designed in such a manner that the alkyl and olefin occupy equivalent coordination sites in *cis* geometry for the active intermediates. To test this hypothesis, herein we designed a  $Ru(n) \eta^6$ -arene complex containing a tethered sulfur ligand (3, Chart 1). As shown in the X-ray structure (Fig. 1), the complex adopts a "piano stool" type of coordination geometry, which upon activation should generate two equivalent coordination sites for active migratory insertion. In this study, we focus on the investigation of active species of this complex for ethylene insertion polymerization. To the best of our knowledge, this is the first direct observation of a cationic Ru complex responsible for olefin insertion polymerization.

## **Results and discussion**

For this purpose, complex 3 was synthesized by following similar procedures reported in literature.<sup>11</sup> First, methyl 3-phenylpropyl sulfide was prepared using a literature procedure,<sup>12a</sup> followed by Birch reduction<sup>12b</sup> to afford ligand **3a**. For complexation, RuCl<sub>3</sub>(hydrate) and **3a** were heated to reflux in ethanol to form **3** as an orange powder (Scheme 1). Complex **3** was fully characterized using <sup>1</sup>H and <sup>13</sup>C-NMR including COSY and NOE experiments, electrospray ionization mass spectrometry (ESI-MS), elemental analysis, and X-ray crystallography (see ESI, Fig. S1–S7†). An analogous dialkylruthenium(II)  $\eta^6$ -arene complex with a tethered phosphine ligand was reported previously, which was inactive for ethylene polymerization.<sup>13</sup>

A single crystal of complex 3 suitable for X-ray diffraction was obtained by slow diffusion of hexanes into a solution of 3 in dichloromethane (DCM) at 4 °C. The X-ray structure of 3 in ORTEP is shown in Fig. 1. Due to the chirality of the sulfur atom, complex 3 exists as a mixture of two enantiomers in the unit cell (ESI Fig. S7†). The sulfide arm remains coordinated to



**Fig. 1** X-ray crystal structure of complex **3**. ORTEP drawing, ellipsoids at 60% probability radius, hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (°): Cl(1)-Ru(1) = 2.4032(1), Cl(2)-Ru(1) = 2.4228(1), S(1)-Ru(1) = 2.3670(1), Cl(1)-Ru(1)-Cl(2) = 86.88(0).



ruthenium in solution as evidenced by the diastereotopic arene and tethered arm protons observed in the <sup>1</sup>H-NMR spectra (ESI Fig. S1–S7<sup>†</sup>). On the basis of variable temperature NMR data, the inversion barrier on sulfur was estimated to be 14.4  $\pm$ 0.1 kcal mol<sup>-1</sup> (see ESI for details<sup>†</sup>), which is close to the inversion barrier for a tetramethylcyclopentadienyl-*S*-tethered cobalt complex reported previously.<sup>14</sup>

Complex 3 was tested for ethylene polymerization using AlMe<sub>2</sub>Cl as the co-catalyst (Table 1). Encouragingly, upon activation complex 3 exhibited moderate activity for producing linear polyethylene.

The polymerization result is reproducible (entries 1 and 2 in Table 1). Increasing ethylene pressure resulted in an increase in molecular weight and a decrease in branching density (entry 3). The polyethylene samples obtained are semicrystalline with melting temperatures ( $T_{\rm m}$ ) around 130 °C. Gel permeation chromatography (GPC) revealed bimodal molecular weight distribution with a high molecular weight fraction ( $M_{\rm n} > 2 \times 10^5 \text{ g mol}^{-1}$ ) and a significantly lower molecular weight fraction ( $M_{\rm n} \sim 600$ –850 g mol<sup>-1</sup>), suggesting the presence of two different active species. As a negative control, a blank polymerization with only AlMe<sub>2</sub>Cl co-catalyst did not produce any polyethylene (entry 4), indicating that the ruthenium complex is critical for active polymerization.

To further probe the active species for the polymerization, we synthesized dimethylated complex 4 *via* direct methylation of 3 with MeLi (Scheme 2). Complex 4 was fully characterized using <sup>1</sup>H and <sup>13</sup>C-NMR including COSY, HMQC and NOE experiments, ESI-MS, and X-ray crystallography (Fig. 2 and ESI Fig. S8–S13†). Similar to 3, complex 4 exists as a mixture of two enantiomers in the unit cell (ESI Fig. S14†). The sulfide arm remains coordinated to ruthenium in solution as evidenced by the diastereotopic arene and tethered arm protons in the <sup>1</sup>H-NMR spectra (ESI Fig. S8†).

Complex 4 can be mono-demethylated by treating it with a stoichiometric amount of a strong acid to generate the proposed cationic active species. In our study, we used 1 eq. of the Brookhart oxonium acid,<sup>2a</sup>  $[H(Et_2O)_2]^+ [BAr'_4]^-$  (where Ar' = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), to protonate complex 4 and remove one methyl group. Upon exposure to ethylene, the mono-demethylated complex exhibited activity for polymerizing ethylene. Similar to polymerization with the 3/AlMe<sub>2</sub>Cl system, higher ethylene pressure resulted in higher activity and lower branching density. As a control, exposure of only ( $[H(Et_2O)_2]^+ [BAr'_4]^-$ ) to ethylene in the absence of complex 4 did not yield any polymer (entry 8), proving again that the ruthenium complex is the active species responsible for ethylene polymerization. The structure of the polymer obtained with  $4/([H(Et_2O)_2]^+ [BAr'_4]^-)$  was

Table 1 Ethylene polymerization results<sup>a</sup>

Entry	Cat.	Co-cat.	$\operatorname{Time}^{b}(h)$	Pressure <sup>c</sup> (psi)	$M_{\rm n}^{\ d}$	$PDI^{e}$	$T_{\mathbf{m}}^{f}(^{\circ}\mathbf{C})$	Branching <sup>g</sup> (Me/1000C)	$\mathrm{TOF}^{h}\left(\mathrm{h}^{-1} ight)$
1 <sup><i>i</i></sup>	3	AlMe <sub>2</sub> Cl	4	400	198 000/638 <sup>j</sup>	$2.03/1.27^{j}$	129	18	22.3
$2^{i}$	3	AlMe <sub>2</sub> Cl	4	400	$214\ 000/646^{j}$	$3.01/1.06^{j}$	130	20	25.3
$3^i$	3	AlMe <sub>2</sub> Cl	12	800	262 000/848 $^j$	$3.03/1.15^{j}$	131	8	46.1
4	_	AlMe <sub>2</sub> Cl	4	400	n/a	n/a	n/a	n/a	0
$5^k$	4	$HBArF^{l}$	12	400	610	1.19	61	36	1.5
$6^k$	4	$HBArF^{l}$	12	800	656	1.23	75	27	3.0
$7^k$	4	$HBArF^{l}$	12	800	657	1.17	69	26	2.8
8	—	$HBArF^{l}$	12	800	n/a	n/a	n/a	n/a	0

<sup>*a*</sup> General conditions: all polymerizations run in a 600 mL Parr reactor with 100 mL of dichloromethane (DCM) as the solvent. Temperature was kept 45–50 °C. <sup>*b*</sup> Hours. <sup>*c*</sup> Ethylene pressure. <sup>*d*</sup> Determined using GPC in 1,2,4-trichlorobenzene *vs.* polyethylene standards. <sup>*e*</sup> PDI =  $M_w/M_{nr}$ . <sup>*f*</sup> Determine using DSC in °C. <sup>*g*</sup> Determined using <sup>1</sup>H-NMR and expressed as the number of Me's per 1000 carbons. <sup>*h*</sup> TOF calculated assuming all Ru is active. <sup>*i*</sup> 6 µmol of complex 3 and 1000 equivalents of AlMe<sub>2</sub>Cl (1.0 M solution in hexanes) as co-catalyst. <sup>*j*</sup> Bimodal distribution. <sup>*k*</sup> 55 µmol of complex 4 and ([H(Et<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> [BAr'<sub>4</sub>]<sup>-</sup>) (1 eq.) as co-catalyst. <sup>*l*</sup> HBArF = ([H(Et<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> [BAr'<sub>4</sub>]<sup>-</sup>) entries 4 and 8 are negative control polymerizations with only AlMe<sub>2</sub>Cl and ([H(Et<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> [BAr'<sub>4</sub>]<sup>-</sup>) respectively.



Scheme 2 Synthesis of complex 4.



**Fig. 2** X-Ray crystal structure of **4**. ORTEP drawing, ellipsoids at 60% probability radius, hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (°): C(12)-Ru(1) = 2.204(1), S(1)-Ru(1) = 2.3187(4), C(11)-Ru(1) = 2.141(2).

identified as polyethylene through <sup>1</sup>H-NMR analysis. GPC traces of polymers made with the  $4/([H(Et_2O)_2]^+ [BAr'_4]^-)$  system are monomodal with molecular weights and PDIs very similar to the low molecular weight fraction of polyethylene obtained with the 3/AlMe<sub>2</sub>Cl system (ESI, Fig. S40 and S41<sup>+</sup>), suggesting that the low molecular weight polyethylene could be produced by the same active species for both the 3/AlMe<sub>2</sub>Cl and 4/  $([H(Et_2O)_2]^+ [BAr'_4]^-)$  systems. The relatively low molecular weight of polyethylene could be due to the low activity and facile chain transfer of catalysts 3 and 4 which lack steric bulkiness. In the case of polymerizations with the 3/AlMe<sub>2</sub>Cl system, a much high molecular weight polyethylene was also formed, presumably by a different active species with an unknown structure. The elucidation of the active species in such aluminium alkyl activated systems remains an unsolved challenge in the coordination polymerization field. Similar to our observation, large

discrepancies between activity and molecular weight were also observed in early transition metal polymerization catalysts between well-defined cationic species and aluminium alkyl activated systems. For example, in Jordan's seminal work on a well-defined Cp<sub>2</sub>ZrMe(THF)<sup>+</sup> system for ethylene polymerization, the activity was ~430 turnovers per hour and the  $M_n$  was ~7130 g mol<sup>-1</sup>,<sup>15</sup> both of which are orders of magnitude lower than for Cp<sub>2</sub>ZrCl<sub>2</sub>/aluminum alkyl activated polymerization.<sup>16</sup> Other studies have also shown that both polymerization activity and polyolefin molecular weight depend significantly on the cocatalyst used.<sup>17</sup> One possibility for our 3/AlMe<sub>2</sub>Cl system is the formation of a small amount of highly active Cl-bridged or clustered species contributing to the formation of high molecular weight polyethylene. Similar halogen-bridged species of this type have been previously reported.<sup>18</sup>

To further investigate the active species contributing to ethylene polymerization, we monitored the initial ethylene binding and subsequent migratory insertion to the *in situ* generated cationic Ru species using low temperature <sup>1</sup>H-NMR. For this purpose, dimethylated complex 4 was added to ethylene-saturated  $CD_2Cl_2$  solution at -78 °C. Addition of one equivalent of  $[H(Et_2O)_2]^+$  [BAr'\_4]<sup>-</sup> (Scheme 3) cleaves one methyl group to generate the active cationic species, complex 5. Low temperature <sup>1</sup>H-NMR (from -90 to 25 °C, ESI Fig. S15–S27†) shows that complex 5 exists as two different diastereomers (5A major and 5B minor, Scheme 3) due to the chirality of the sulfur atom. Based on the NMR integrations, the two species are present in a 4 : 1 ratio at -90 °C. Density function theory (DFT) calculations confirm that complex 5A is the major species because it has less steric repulsion between the S-CH<sub>3</sub> methyl



Scheme 3 In situ activation and initial ethylene binding to the Ru complex 4.

group and the ethylene bound to Ru. In the minor complex (5B), ethylene coordinates on the same side as the methyl group, resulting in higher steric repulsion. A number of NMR techniques, including COSY, HMQC, and NOE experiments, were employed to investigate the active species (ESI Fig. S15–S27†). The ethylene coordinated to the cationic Ru species in complex 5 was observed at -90 °C with no free rotation, affording four proton signals from 4.0 ppm to 1.5 ppm. At -10 °C, the two diastereomers re-equilibrated to a ratio of 5A : 5B  $\sim 2$  : 1. Upon further warming, the ethylene proton signals coalesced to give two doublets centered at 2.9 ppm. At 25 °C, the two sets of peaks from the two diastereomers coalesced into one set of broad peaks due to dynamic exchange, precluding detailed structural analysis. At 45 °C, the Ru–Me peaks started to disappear and the <sup>1</sup>H-NMR spectrum became more complex (see ESI, Fig. S28†).

The initial migratory insertion barrier was determined by monitoring Ru-Me peak disappearance.<sup>2c</sup> The first insertion was observed at 288 K at a very slow rate (ESI Fig. S33<sup>†</sup>). As mentioned above, complex 5 exists in two diastereomers, 5a and 5b. The Ru-Me peak for the major isomer, 5a, significantly overlaps with those of the growing oligomers, precluding quantitative integration of the signal (ESI Fig. S34<sup>†</sup>). Therefore, the Ru-Me peak of the minor isomer, 5b, was chosen for kinetic analysis. We determined the initial migratory insertion barrier by monitoring Ru-Me first-order disappearance for 5b at 301 K for a period of 6 h. The initial migratory insertion barrier was calculated to be 22.8  $\pm$  0.1 kcal mol<sup>-1</sup> at 301 K (ESI Fig. S35†), which is significantly lower than the calculated barriers for complexes 1 and 2.9 Free ethylene consumption was also monitored, which correlates well with Ru-Me disappearance (ESI Fig. S36 and S37<sup>†</sup>). Monitoring the growth of oligomers was complicated by rapid β-hydrogen elimination and chain transfer as well as by peak overlaps.

The same solution used for these aforementioned NMR studies was heated to 45 °C (318.15 K) for 15 minutes and then subjected to electrospray mass spectrometry (ESI-MS) analysis of species existing in the solution (Fig. 3). The ESI-MS spectrum unambiguously confirmed that migratory insertion indeed occurred on cationic ruthenium species 5. Two series of growing oligomers were observed in the spectrum with increasing numbers of ethylene insertion. In one series of peaks, the number of carbons in the alkyl chain is odd (n = 1, n)3, 5, 7, Fig. 3, blue dots), which resulted from primary ethylene insertion to complex 5. In another series of peaks, the number of carbons in the alkyl chain is even (n = 0, 2, 4, 6, Fig. 3, red)dots), which presumably formed by ethylene insertion after chain transfer to the Ru center occurred (see ESI Fig. S29-S31 for detailed analysis<sup>†</sup>). The isotopic pattern for each peak agrees well with the molecular formula for each oligomeric species. Interestingly, an almost identical ESI-MS spectrum was obtained when the 3/AlMe<sub>2</sub>Cl system was exposed to ethylene (1 atm at 45 °C for five minutes, in ESI Fig. S32<sup>†</sup>), confirming that at least one of the active species (low molecular weight fraction) in the 3/AlMe<sub>2</sub>Cl system is the same as in the  $4/[H(Et_2O)_2]^+$  system. Both our NMR and ESI-MS data confirm that the ruthenium is the active centre where the polymer chain grows.



**Fig. 3** ESI-MS spectrum of the *in situ* polymerization sample. Several growing oligomeric species were identified due to successive ethylene insertion to the cationic Ru center. Blue circles indicate oligomers resulting from primary ethylene insertion to complex **5**. Red circles indicate oligomers formed from ethylene insertion to  $Ru(H)^+$  species generated from chain transfer. Detailed analysis and comparison with simulated isotopic patterns are available in the ESI.<sup>†</sup>

## Conclusions

In conclusion, we have designed and synthesized a novel ruthenium n<sup>6</sup>-arene complex with a tethered sulfur ligand that is capable of catalyzing ethylene insertion polymerization. The structures of the Ru complexes were fully characterized using NMR, ESI-MS, elemental analysis, and X-ray crystallography. Complexes 3 and 4 adopt a "piano stool" type of coordination geometry, which upon activation generates two equivalent coordination sites for active migratory insertion. The active catalytic species was investigated using low temperature <sup>1</sup>H-NMR and mass spectrometry. Our results have unambiguously established that the cationic ruthenium is the active species for ethylene insertion polymerization. The initial migratory insertion barrier was determined to be  $\sim$ 22.8  $\pm$  0.1 kcal mol<sup>-1</sup> at 301 K, a barrier significantly higher than that of the nickel- and palladium-a-diimine system<sup>2,4c</sup> but lower than the calculated barriers for previous ruthenium complexes 1 and 2.9 To the best of our knowledge, this is first direct observation of a cationic Ru complex responsible for olefin insertion polymerization. A number of other Ru complexes are currently under investigation in our laboratory for both ethylene homopolymerization and copolymerization with polar olefins.

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