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# COMMUNICATION

# A ruthenium catalyst yielding crosslinked polyethylene†

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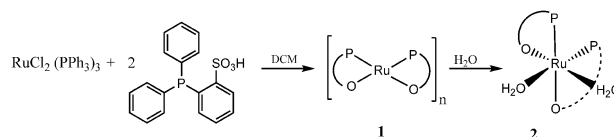
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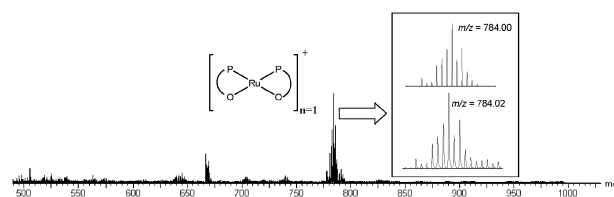
**A ruthenium phosphane aryl sulfonate was found to be an efficient catalyst for the polymerization of ethene. Surprisingly, the resulting polyethylene is crosslinked.**

More than 50 years after the discovery of Ziegler and Natta on olefin polymerization, the quest for insertion-coordination catalysts capable of providing extended control over the polymer structure is still ongoing.<sup>1</sup> Olefin polymerization catalyzed by late transition metals has attracted much interest and opened the way to a myriad of new catalysts.<sup>2</sup> These catalysts are not only more robust towards impurities, but also allow the copolymerization of ethene with polar monomers. The majority of those catalysts are based on Ni and Pd, but a major advance was reported by Brookhart *et al.*<sup>3</sup> and Gibson *et al.*<sup>4</sup> who simultaneously discovered very active bis(imino)pyridine Fe and Co precatalysts which can polymerize ethene in the presence of methylaluminoxane (MAO) with activities comparable to the Ziegler–Natta system. By contrast to Ni, Pd, Fe and Co, the reactivity of Ru complexes in insertion polymerization has hardly been scrutinized. Nomura *et al.* have reported that Ru complexes bearing bis(oxazoline)pyridine (pybox) ligands show very low activity for the polymerization of ethene upon activation with MAO (TON = 75 mol ethene per mol Ru).<sup>5</sup> Dias *et al.* have demonstrated that bis(imino)pyridine Ru cationic alkyl complexes show no activity towards ethene insertion.<sup>6</sup>

Since ruthenium possesses excellent functional group tolerance in olefin metathesis and has low moisture and air-sensitivities,<sup>7</sup> while being approximately one-third the price of palladium per mole, it would be very advantageous to develop Ru polymerization catalysts containing phosphane aryl sulfonate ligands with selectivities identical to those encountered with Pd. Indeed, phosphane aryl sulfonate Pd complexes exhibit unprecedented versatility, permitting the copolymerization of ethene with a wide variety of polar olefins.<sup>8,9</sup> To our knowledge, phosphane aryl sulfonate Ru polymerization catalysts have never been reported, but recently it has been shown that Ru(IV) complexes bearing phosphane aryl sulfonate ligands can be used for



**Scheme 1** Ruthenium phosphane aryl sulfonate complexes.



**Fig. 1** MALDI TOF mass spectrum of **1** (anthracene matrix, dichloromethane). Insets show isotope patterns for the molecular ion (top: simulated, bottom: observed).

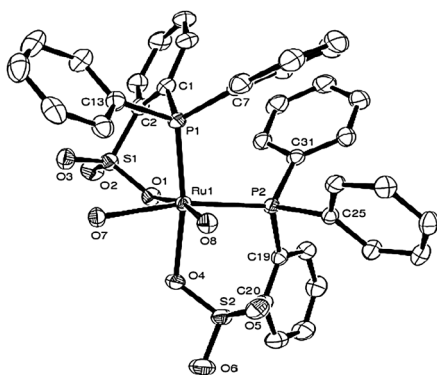
catalytic regioselective allylation reactions.<sup>10</sup> We report herein a Ru phosphane aryl sulfonate complex that is active for the preparation of high-density polyethylene.

Aryl sulfonate phosphane complex **1** was prepared in 87% yield by reaction of two equivalents of the aryl sulfonate phosphane ligand with  $\text{RuCl}_2(\text{PPh}_3)_3$  in dichloromethane (Scheme 1). The  $^{31}\text{P}$  NMR of the reaction mixture showed the disappearance of the signals corresponding to the starting materials and appearance of a new singlet at 27 ppm implying a symmetrical structure. Analogous reactions with  $\text{RuCl}_3$ ,  $[\text{RuCl}_2(\text{COD})]_n$ , or  $\text{RuCl}_2(\text{DMSO})_4$  as starting material generated again complex **1** but in lower yields. The elemental analysis of this orange compound agrees with the formula  $\text{Ru}(-\text{PPh}_2-\text{C}_6\text{H}_4-\text{SO}_3^-)_2$ . Thus, **1** is a dimeric or polymeric complex whereby bridging occurs *via* sulfonate units, as already reported in the case of Pd.<sup>11</sup> Further evidence for the structure was suggested from a matrix-assisted laser desorption/ionization time of flight MALDI-TOF MS study of this compound in dichloromethane (Fig. 1).<sup>12</sup> In this case, only the monomeric form of **1** is detected.

Complex **1** reacts in the presence of water to form the well-defined mononuclear species **2** which can be crystallized from a layered acetone–water (1 : 1) solution (Fig. 2). The structure can be described as a distorted octahedron with the PRuP angle being significantly larger than 90° and O7–Ru–O8 angle being smaller than 90°, probably as a consequence of the bulk of the aryl phosphane groups. Accordingly, bulkier *o*-sulfonated phosphanes Ar<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H where Ar = Ph(*o*-OMe) or Ar = Ph[*o*-C<sub>6</sub>H<sub>3</sub>(2,6-OMe)<sub>2</sub>] only reacted in less than 10%

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**Fig. 2** Thermal ellipsoids diagram (50%) of **2**. All hydrogen atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (°): Ru–P1 2.272(5), Ru–P2 2.281(5), Ru–O1 2.126(2), Ru–O4 2.176(1); O(1)–Ru–O(8) 168.91(6), P(1)–Ru–P(2) 98.57 (2), P(1)–Ru–O(4) 171.07(4), O(1)–Ru–P(1) 92.36(4), O(8)–Ru–O(7) 84.18(6), O(1)–Ru–P(2) 93.27(4).

yield with  $\text{RuCl}_2(\text{PPh}_3)_3$  to form analogous Ru complexes. This is consistent with the important steric strain generated by the two chelating phosphanes in an octahedral environment. The six membered cycles  $\text{Ru}(1)\text{--P}(1)\text{--C}(1)\text{=C}(2)\text{--S}(1)\text{--O}(1)\text{--}$  and  $\text{Ru}(1)\text{--P}(2)\text{--C}(19)\text{=C}(20)\text{--S}(2)\text{--O}(4)\text{--}$  adopt a half-boat conformation, with C(25) C(13) O(3) and O(5) in pseudo axial positions and C(31) C(7) O(2) and O(6) in pseudo equatorial positions. This half boat conformation has been reported for the majority of aryl sulfonate catalysts.<sup>9c,e,h,13</sup> It is surprising that the phosphane moieties are *cis* to each other as these ligands with a strong *trans* influence are expected to prefer *trans* positions with respect to each other.

The results of ethene polymerization are consigned in Table 1. The optimal conditions for polymerization were found to be

**Table 1** Ethene polymerization by Ru catalysts<sup>a</sup>

Run no.	Complex/ μmol	Cocatalyst <sup>b</sup> [Al/Ru]	T/°C	Ethene/ atm	TON/ mole per mol <sub>Ru</sub>
1	<b>1</b> (5)	1600	65 <sup>c</sup>	20	2270
2	<b>2</b> (5)	300	50	20	560
3	<b>2</b> (5)	300	80	20	696
4	<b>1</b> (5)	300	95	20	505
5	<b>1</b> (6)	150	65	7.5	316
6	<b>1</b> (6)	300	65	7.5	392
7	<b>2</b> (5)	900	65	7.5	255
8	<b>2</b> (6)	1300	65	7.5	239
9	<b>1</b> (10)	800	80	20	32 <sup>d</sup>
10	<b>1</b> (10)	800	80	20	403 <sup>c</sup>
11	<b>1</b> (10)	800	110	20	122
12	<b>1</b> (10)	800	125	20	54
13	<b>2</b> (5)	0	65	3.4	—
14 <sup>b</sup>	<b>2</b> (5)	300	65	14	—
15	(5) <sup>f</sup>	300	65	3.4	—
16 <sup>g</sup>	<b>2</b> (5)	300	80	20	1110
17 <sup>h</sup>	<b>2</b> (5)	150	65	20	340

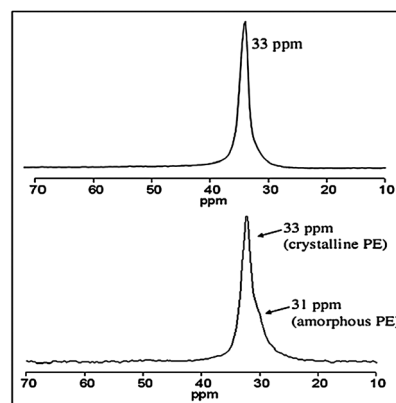
<sup>a</sup> Reaction conditions: solvent = toluene (50 mL) overnight. <sup>b</sup> Molar ratio of Al/Ru, cocatalyst is MAO except for run 14, for which it is  $\text{AlEt}_3$ . <sup>c</sup> An important exotherm was observed. <sup>d</sup> Reaction time = 30 minutes. <sup>e</sup> Reaction time = 180 minutes. <sup>f</sup> 5 μmol of ligand was used instead of complex **1**. <sup>g</sup> 2.5 mL of hexene was added. <sup>h</sup> 2.5 g of norbornene was added.

65 °C (run 1) at higher ethene pressure (comparing runs 2–4 to runs 5–8). Above 95 °C, catalyst activity decreases (runs 10–12), due to catalyst decomposition. Overall, the polymerizations were sluggish. After 30 minutes (run 9) only a minute amount of polymer was isolated. Consequently, polymerizations were conducted overnight. Control experiments involving Ru complex **1** without MAO (run 13), **1** with an aluminium alkyl (run 14) and ligand + MAO without any Ru source (run 15) only yielded trace amounts of solid material. Interestingly, polymerizations performed with precatalysts **1** or **2** gave similar results, both in terms of activity and polymer microstructure, and these two compounds were used interchangeably. These precatalysts are also very stable, and can even be stored in air at room temperature.

Most surprisingly, the resulting polymer does not appear to be fully soluble, even when gently stirred at 160 °C in trichlorobenzene, TCB, for 24 hours, conditions under which even ultra high molecular weight polyethylene is solubilized.<sup>14</sup> Evidence that the solid collected is indeed polyethylene stems from solid-state  $^{13}\text{C}$  NMR using magic-angle spinning (MAS) cross-polarization (CP) and direct polarization (DP) sequences (Fig. 3). The main resonance corresponds to crystalline polyethylene, whereas the small one convoluted in the main peak corresponds to amorphous polyethylene.<sup>15</sup> Importantly, no other peak could be detected by solid-state NMR, indicating that the polymer is 'linear' polyethylene. This is also confirmed by the presence of a high melting point (136 °C) as measured by differential scanning calorimetry (DSC).

Since the polymer is not totally soluble, we have decided to measure its gel content (portion of polymer insoluble in the solvent) and its degree of swelling (which is the volume fraction of the swollen gel divided by the volume fraction of the dried gel). Analysis by high-temperature GPC has indicated that less than 20% of each polymer sample is soluble at 160 °C in TCB (based on integration by differential refractometer). Thus, gel content is higher than 80% for each sample. The degree of swelling in xylene at 125 °C after 48 hours was 15, 12 and 18, respectively, for polymers from runs 1, 4 and 6, corresponding to a molecular weight of  $10^4$  to  $4 \times 10^4$  g mol<sup>−1</sup> between two crosslinks. Therefore, the polymer is only slightly crosslinked.

Only for runs 1 and 6, the soluble fraction of the polymer was in sufficient amount to be analyzed by GPC. By comparing



**Fig. 3**  $^{13}\text{C}$  CP/MAS (above) and  $^{13}\text{C}$  DP/MAS (below) Solid State NMR spectra of polyethylene (run 1).

the number average degree of polymerization ( $X_n = 21\,800$  for run 1, 12 400 for run 6) to the ethene to catalyst ratio (2270 for run 1, 316 for run 6), it is clear that only a small fraction of the Ru is active. Interestingly, the soluble portion of run 1, analyzed by triple detection GPC has a high molecular weight ( $M_n = 610\,000\text{ g mol}^{-1}$ ,  $M_w/M_n = 1.3$ ). The Mark-Houwink plot is linear, with a slope of 0.75 which corresponds to the plot of a polyethylene devoid of short branches. The absence of branches on the soluble portion of the polymer is consistent with the fact that the polymer is only slightly crosslinked.

When a preformed linear polyethylene sample ( $M_n = 15\,400\text{ g mol}^{-1}$ , PDI = 1.5) is contacted with the catalytic system (**1** and 200 eq MAO, 80 °C overnight) in the absence of ethene, its molecular weight distribution remains unchanged, indicating that crosslinking occurs concomitantly to the formation of the polymer. Attempts to isolate an uncrosslinked polymer in the early stages of the reaction failed. When a polymerization was stopped after 30 minutes (run 9), the amount of polymer was insufficient for solubility testing and GPC analysis, but after 3 hour reaction time (run 10), the polymer was already found to be crosslinked.

One possibility to account for crosslinking is that the initiation step yields a growing chain metallated at both ends. After successive insertions and  $\beta$ -H elimination, an  $\alpha$ - $\omega$  olefin is obtained. Reinsertion of this difunctional macromonomer could then be responsible for the presence of crosslinks. Such a mechanism would entail that  $\alpha$ -olefins are incorporated by the Ru catalysts. Copolymerization of ethene and hexene catalyzed by **1** generates again an insoluble copolymer with a melting point of 88 °C, as measured by DSC, indicating that this catalyst is capable of inserting hexene, however, we were not able to homopolymerize hexene with these catalysts. Although the suggested crosslinking mechanism is probable (but difficult to further elucidate due to the insoluble nature of the polymer), it is important to mention that in a recent paper, using DFT calculations, Heyndrickx and co-workers concluded that the classical Cossee-Arlman mechanism is improbable for low activity (pybox)RuCl<sub>2</sub>(ethene) catalysts.<sup>16</sup> Copolymerization of ethene with norbornene by **1** was also performed. Once again, a cross-linked polymer was obtained and importantly no trace of soluble ROMP polynorbornene was detected by <sup>1</sup>H NMR.

To conclude, we found the first example of a significantly active homogeneous ruthenium catalyst for the polymerization of ethene. Based on the analysis of the soluble fraction of the polymer, the catalyst generates high molecular weight polyethylene devoid of short branches. However, this polyethylene is crosslinked. This surprising finding has interesting repercussions for the preparation of novel polyolefins with unusual macromolecular architectures<sup>17</sup> and more importantly it addresses new mechanistic avenues concerning the reactivity of alkyl Ru complexes. In polymerization catalysis, it is often considered

that Ru is suitable for ROMP only (even RuCl<sub>3</sub>·xH<sub>2</sub>O is an efficient catalyst for the ROMP of norbornene!<sup>18</sup>) but our finding offers a contrasted view of the reactivity of Ru complexes.

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