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$(C_5H_5)_2TiF_2$ and $(C_5H_5)_2ZrF_2$ as catalyst precursors for the dehydropolymerisation of silanes

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Abstract

$(C_5H_5)_2TiF_2$ and $(C_5H_5)_2ZrF_2$ were found to be rapidly converted into catalytically-active species for the dehydrocoupling of silanes upon treatment with $PhSiH_3$ or $H_2MeSiSiMeH_2$. © 1998 Elsevier Science S.A. All rights reserved.

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In the catalytic dehydropolymerisation with Group IV metallocenes a number of catalyst precursors are known so far. Most of them are air and moisture sensitive like $(C_5H_5)_2M(Me)Si(SiMe_3)_3$ [1] $(C_5H_5)_2M(BTMSA)$ [2] or have to be pre-prepared for each reaction like $(C_5H_5)_2MCl_2/2BuLi$ [3] ($M = Ti, Zr$) the latter being a highly complex and ill defined system [4]. Although $(C_5H_5)_2MMe_2$ compounds lack the mentioned disadvantages they have to be stored at low temperature and have varying induction periods [5]. Buchwald et al. recently reported on the conversion of $(C_5H_5)_2TiF_2$ to a titanium(III) hydride by treatment with $PhSiH_3$ [6]. As metallocene hydrides are known to be catalytically active species in the dehydropolymerisation of silanes [1], we decided to study the use of $(C_5H_5)_2TiF_2$ and also $(C_5H_5)_2ZrF_2$ as catalysts for the polymerisation of $PhSiH_3$ and $H_2MeSiSiMeH_2$.

When $(C_5H_5)_2TiF_2$ was added to neat $PhSiH_3$ the metallocene started to dissolve and yielded a vigorously bubbling dark blue solution [6]. The reaction continued to proceed at room temperature (r.t.) and solidified after 5 h. When the solid polymer was dissolved in toluene hydrogen evolution could still be observed. In the course of 1 week, the reaction slowly lost its blue colour and turned yellow brown, and the gas evolution ceased completely. Removal of the volatiles yielded a brittle, yellow solid ($M_n = 1040$ Da, $M_w = 1620$ Da) (Fig. 1). As usually observed with Ti catalysts a substantial fraction of cyclic products of about 30% was formed. Treatment of $(C_5H_5)_2TiF_2$ with $H_2MeSiSiMeH_2$ and heating shortly to reflux also yielded a gas evolving solution with the above described colour. The reaction solidified after 3 days at r.t., resulting a completely insoluble, yellow–green polymer.

The conversion of $(C_5H_5)_2ZrF_2$ into a catalytically active species required longer induction periods and higher temperatures than its Ti analogue. The reaction with $PhSiH_3$ yielded a bright yellow solution and the gas evolution was weaker than with $(C_5H_5)_2TiF_2$. After 3 days reaction at r.t., an oily yellow polymer was obtained ($M_n = 1400$ Da, $M_w = 2200$ Da) (Fig. 1). The fraction of cycles was $< 10\%$. The polymerisation also proceeded in the presence of diethylamine affording poly(diethylamino)phenylsilane. ^{1}H-NMR data of the polysilane shows that the degree of incorporation of NEt_2 groups is about 50% (Fig. 1) [7]. When a suspension of $(C_5H_5)_2ZrF_2$ in $H_2MeSiSiMeH_2$ was heated to the boiling point of the silane, only a small proportion of the metallocene dissolved and yielded a slightly

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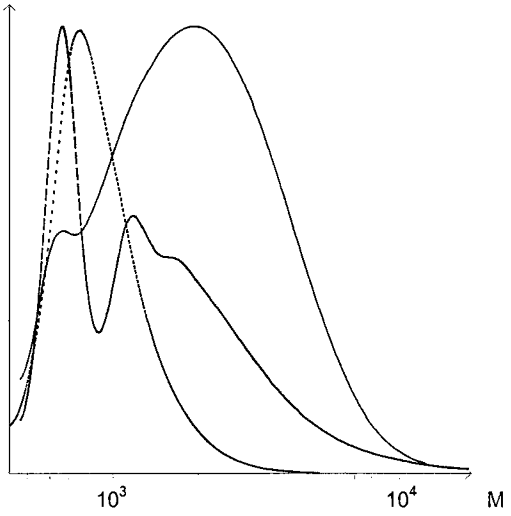

Fig. 1. Molecular weights of the obtained polymers versus polystyrol standards. (– – –) $PhSiH_3 + (C_5H_5)_2TiF_2$, (—) $PhSiH_3 + (C_5H_5)_2ZrF_2$, (--- -) $PhSiH_3 + HN(Et)_2 + (C_5H_5)_2ZrF_2$.

bubbling yellow solution. After 1 h reaction at r.t. the gas evolution ceased. Analysis by GC/MS showed that only tri- and tetrasilane were formed to a significant extent after 2 days at r.t.

The driving force for the formation of metallocene hydrides by fluoride–hydride exchange between metal and silane seems to be the formation of an extraordinary stable Si–F bond [6]. Once the metallocene difluoride is transformed into a soluble species by this exchange reaction the following metathesis steps start the polymerisation immediately without any induction period. As metallocene fluorides are stable to light, air and moisture and can be stored at r.t. they appear to be very interesting as catalyst precursors.

To test the hypothesis that the actual catalyst in the described reactions is a M (III) species, which would be supported by the sluggish reaction of $(C_5H_5)_2ZrF_2$ we studied the reaction of $(C_5H_5)_2TiF_2$ with $PhSiH_3$ using EPR spectroscopy. We observed a doublet of triplets at $g = 1.9924$ with the coupling constants $a_{H(1)} = 1.553$ mT (1 H) and $a_{H(2)} = 0.944$ mT (2 H) which was assigned to $[(\eta^5\text{-}C_5H_5)_2TiH]_2(\mu\text{-}H)$ by Harrod [8,9] and a non-resolved radical at $g = 1.9722$ (Fig. 2). On grounds of our experimental evidence we could not decide whether the observed Ti (III) compounds are part of the catalytic cycle or not [10]. Nevertheless the intensity of the EPR signals indicated that only a small proportion of $(C_5H_5)_2TiF_2$ was reduced to a paramagnetic species. The reaction of $(C_5H_5)_2ZrF_2$ with phenylsilane did not produce any observable radicals at all which could be detected by EPR spectroscopy although the reaction proceeded with vigorous bubbling and the characteristic bright yellow colour at 60°C. In the case of the $(C_5H_5)_2ZrF_2$-initiated reaction, a Zr (III) species as the true catalyst becomes very improbable in the light of these findings.

Further work with $(C_5H_5)(C_5Me_5)MF_2$ compounds is planned in order to isolate intermediate products which should be helpful in the elucidation of the reaction mechanism and the nature of the catalytically active species.

1. Experimental

$(C_5H_5)_2TiF_2$ and $(C_5H_5)_2ZrF_2$ were synthesised according to literature procedures [11]. $PhSiH_3$ was obtained by LAH reduction of $PhSiCl_3$ in ether, followed

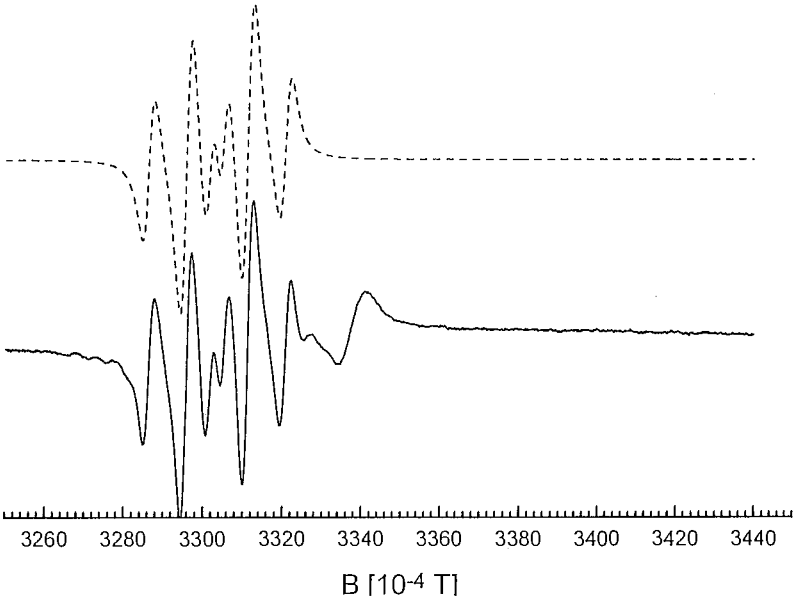

Fig. 2. (—) EPR spectrum of $(C_5H_5)_2TiF_2 + 2PhSiH_3$ in toluene. (---) Simulation [$a_{H(1)} = 1.544$ mT (1 H), $a_{H(2)} = 0.947$ mT (2 H)].

by aqueous acidic workup and distillation. In a similar fashion $H_2MeSiSiMeH_2$ was obtained by LAH reduction of $Cl_2MeSiSiMeCl_2$ [12] in dibutyl ether. However, isolation in the latter case was achived by distillation (b.p. 48°C) of the product from the dibutyl ether solution [13].

The polymerisation experiments were performed in Schlenk tubes under an atmosphere of dry Argon. To 1 ml of silane 1 mol% of catalyst was added. Either at r.t. or upon gentle heating the reaction started, indicated by a dark blue colour of the reaction mixture for the titanium catalysed reactions and a bright yellow colour for its zirconium analogues.

1.1. Copolymerisation of $PhSiH_3$ with diethylamine

A mixture of 1 ml $PhSiH_3$ (8 mmol) and 1 ml diethylamine (10 mmol) was charged with 20 mg of $(C_5H_5)_2ZrF_2$ (0.08 mmol) and refluxed for one day. After removal of the volatiles, a bright yellow solid was obtained. ^{1}H NMR: 6.6–8.3 (10 H), 4.5–6 (1 H), 2.4–3.2 (2 H), 0.6–1.3 ppm (3 H). GPC: $M_n = 830$, $M_w = 950$ Da.

1.2. EPR experiments

A 20 mg sample of $(C_5H_5)_2TiF_2$ was reacted with two equivalents of phenysilane in 100 μl toluene in an EPR tube. The reaction proceeded already at r.t. to produce the cited EPR signals.

$(C_5H_5)_2ZrF_2$ was treated in the same way, but did not react at all at r.t. The temperature was slowly raised. At 40°C a slight bubbling of the colourless solution could be observed, and at 60°C the colour of the reaction mixture turned yellow, the gas evolution became much stronger, but still no EPR signal could be observed.

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