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New palladium α-diimine complexes containing dendritic wedges for ethene oligomerisation

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Abstract

The synthesis of new α-diimine ligands containing zero and first generation dendritic wedges is described. These ligands were reacted with (COD)$PdCl_2$ to give the corresponding palladium α-diimine complexes. The resulting palladium complexes are active in the oligomerisation of ethene and the activity was compared to a related nickel complex.

Keywords: Palladium; α-Diimine ligand; Dendritic wedge; Oligomerisation, Ethene

1. Introduction

The oligomerisation of ethene is one of the major industrial processes for the production of linear 1-alkenes [1]. Oligomers in the range C_6–C_{20} are used as co-monomers in the polymerisation of ethene to give linear low-density polyethene (LLDPE) or for the preparation of detergents and synthetic lubricants. Catalysts currently used in industry for the Shell Higher Olefin Process (SHOP) [2] contain Ni(II) complexes bearing bidentate mono-anionic ligands [1,2]. Cationic Ni(II) α-diimine complexes were also reported to be effective ethene oligomerisation catalysts [3], while iron-based bis(imino)pyridine catalysts were described as highly active compounds in the oligomerisation of ethene in combination with the co-catalyst MAO or MMAO [4]. Several modifications of the bis(imino)pyridine backbone which have already been described in the literature [5] mostly lead to a decrease in catalytic activity. Recently, related fluoro-substituted bis(imino)pyridine complexes of iron and their catalytic reactivity in ethene oligomerisations were described [6], as were bis(imino)pyridine complexes containing methoxy and CF_3 groups [7]. Recently we described iron bis(imino)pyridine complexes containing dendritic wedges for ethene oligomerisation [8]. Here we wish to report the related palladium α-diimine systems containing wedges of the poly(benzylphenyl ether) type.

Since the independent reports by Gibson and Brookhart [9] on nickel and palladium α-diimine catalysts and iron and cobalt bis(imino)pyridyl catalysts for the polymerisation and oligomerisation of 1-alkenes [9], much attention has been focused on these late transition metal catalysts as alternatives to established technologies.

It is known that the position and steric bulk of the substituents on the aryl rings of the α-diimine catalysts (Fig. 1) plays a crucial role in determining the selectivity of the catalyst. In particular, the *ortho* substituents (R_1) have been identified as important. If R_1 is a non-hydrogen substituent, and preferably a bulky substituent such as *iso*-propyl groups, then the resulting catalysts are selective for the production of high molecular weight polymers from ethene. If only one of the two *ortho*

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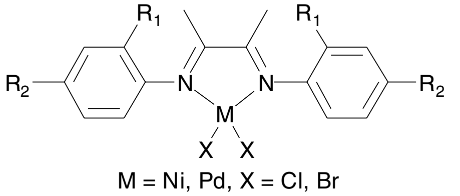


Fig. 1. Palladium and nickel α-diimine catalyst for the oligomerisation of 1-alkenes.

positions R_1 on the aryl rings is an alkyl substituent, the catalyst is selective for the oligomerisation of ethene to linear 1-alkenes with a Schulz-Flory [10] chain length distribution, and for the dimerisation of longer chain olefins (such as 1-hexene). The effect of substituents in the *para*-position (R_2) has been less studied. Our interest in dendritic molecules [11], their applications in catalysis and as new materials, led us to consider the possibility of functionalising late transition metal oligomerisation catalysts with dendritic components. This could take the form of attaching dendritic wedges to the catalysts, thus creating a catalyst at the core of a dendrimer. By having a catalytic site at the core of a dendrimer, it should be possible to control the micro-environment around the catalytic centre and thus allow modifications of the catalytic selectivity [12]. In addition to the latter, dendritically substituted homogeneous catalysts should be easily separated from the product stream by means of ultrafiltration methods.

Functionalising an α-diimine ligand with dendritic wedges to create a catalytic ligand at the core of a dendrimer is likely to be synthetically achievable. The aryl components of the ligand are particularly amenable to dendritic functionalisation, as a wide range of anilines with different functionalities for substitution are commercially available. These may be reacted in standard Schiff-base type reactions with 2,3-butadione to form the α-diimine framework with aryl rings suitable for attachment of dendritic wedges. Dendritic functionalisation at the *para*-position is most favourable. The direct steric control around the catalytic centre may be controlled by appropriate *ortho* substitution (R_1, Fig. 1), thereby ensuring an oligomerisation catalyst. The heteroatomic functionality, for attachment of the dendritic wedges, is introduced on the *para*-position (R_2, Fig. 1) and thus removed from the active catalytic centre in order to minimise unfavourable interactions.

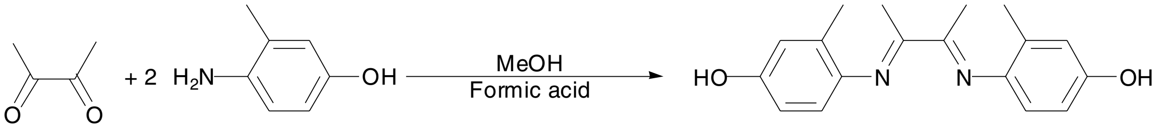
2. Results and discussion

2.1. Preparation of ligands

Appropriate ligands would be α-diimine ligands with either both *ortho*-substituents (R_1, Fig. 1) being hydrogen, or one of the substituents R_1 on each ring being a methyl group and the other a hydrogen. We chose to prepare ligands with one methyl group on the *ortho*-position for this study. Substituent R_2 was chosen to be a hydroxyl group for ease of attachment of alkylbromide functionalised dendritic wedges, using the standard Williamson ether synthesis. Thus compound **1** was synthesised using the simple Schiff-base condensation reaction of 2,3-butadione and two molar equivalents of amino-*m*-cresol (Scheme 1).

The *para*-hydroxyl group allows attachments of various dendritic wedges containing an alkylbromide functionality on the focal point. Using the Williamson ether synthesis, a quantitative yield of dendritically functionalised α-diimine ligands was expected. Fréchet and co-workers reported the quantitative build-up of poly(benzylphenyl ether) dendrimers [13] when applying mild reaction conditions. Applying similar conditions, we reacted two equivalents of the appropriate bromoalkyl wedge with **1** in acetone, heated under reflux, using K_2CO_3 as the base and a sub-stoichiometric amount of 18-crown-6 as phase transfer catalyst (Scheme 2). The reactions typically were allowed to proceed for between 48 and 72 h. The compounds **2** and **3** were separated from the inorganic salts using an aqueous work-up. Analytically pure samples were obtained by recrystallisation from an appropriate solvent. Fréchets poly(benzylphenyl ether) dendritic wedges [13] were chosen because they are easily prepared and react readily with hydroxyaryl compounds. These wedges have previously been used as dendritic catalysts for anionic ring opening polymerisation reactions [14]. We reported the use of these wedges connected to iron bis(imino)pyridyl complexes [8] in alkene oligomerisation previously. Details on the wedges employed are given in Scheme 2.

The ligands **2** and **3** were characterised by ^1H, ^{13}C NMR spectroscopy, IR spectroscopy and satisfactory elemental analysis. For ligand **2**, satisfactory mass spectrometric was obtained and the molecular ion was observed. Ligand **3** unfortunately decomposed under MS



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Scheme 1. Synthesis of **1**.