Tandem reactions of Friedel–Crafts/aldehyde cyclotrimerization catalyzed by an organotungsten Lewis acid

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Abstract—The tris(2-pyridyl)phosphine complex \([\text{P}(2\text{-py})_3\text{W} (\text{CO})(\text{NO})_2]\text{BF}_4\text{)}_2\) acts as a Lewis acid catalyst precursor for the tandem reactions of Friedel–Crafts (F–C)/aldehyde cyclotrimerization, which lead to the formation of a series of hyper-branched star polymers. © 2002 Elsevier Science Ltd. All rights reserved.

There has been considerable recent research interest into the chemistry of low-valent organometallic Lewis acids.1,2 We communicate herein our development of a new process for the catalytic tandem reactions of Friedel–Crafts (F–C)/aldehyde cyclotrimerization by an organotungsten Lewis acid. The process provides a notably efficient method for the one-pot synthesis of a series of hyper-branched star polymers bearing five- and six-membered heterocyclic sub-units from the reactions of five-membered heterocyclic arenes and \(\alpha,\beta\)-unsaturated aldehydes.

The zero-valent tungsten complex \([\text{P}(2\text{-py})_3\text{W} (\text{CO})(\text{NO})_2]\text{BF}_4\text{)}_2\) \(1\) possesses strong Lewis acidity upon loss of the CO ligand, and the relative Lewis acid strength of \(1\) is found to be comparable to those of \(\text{AlCl}_3\) and \(\text{BF}_3\).4 In addition, \(1\) can be easily prepared in two steps with high yield from \(\text{W(CO)}_6\), and can be stored as a crystalline solid in air for months without significant decomposition. The organotungsten Lewis acid \(1\) acts as a catalyst precursor for the synthesis of a series of hyper-branched star polymers. These star polymers are generated from a one-pot reaction process of double F–C alkylation of five-membered heterocyclic arenes with \(\alpha,\beta\)-unsaturated aldehydes followed by cyclotrimerization of the F–C adducts (Scheme 1). These tandem reactions are carried out in neat substrates at ambient temperature with a catalyst loading of 0.05–1 mol% to afford quantitative insoluble polymers almost instantaneously (Table 1). It is most likely that the complex \(1\) catalyzes double F–C alkylation of the five-membered heterocyclic arenes such as furan and pyrrole with acrolein and/or crotonaldehyde at both C-2 and C-5 positions during the course of the tandem reactions. Subsequently, two aldehydic end groups at both sides of the F–C adducts undergo further catalytic cyclotrimerization to afford the hyper-branched star polymers consisting of five- and six-membered heterocyclic sub-units.

To verify the initiation and propagation steps for the formation of these hyper-branched star polymers, two separate controlled experiments are conducted. In the first experiment,5 methyl vinyl ketone (MVK) is treated with the reactant arenes such as furan, pyrrol and thiophene in the presence of 1 mol% of \(1\). As expected, the reactions undergo double F–C alkylation to give the corresponding 2,5-disubstituted arenes in quantitative yields (Scheme 2A). Besides, there are no other detectable by-products such as mono- and 2,4-disubstituted adducts formed. In the second experiment, a series of aldehydes \(\text{RCOH (R = Me, Et, n-Pr, i-Pr, n-Bu)}\) are used straight without solvents in the presence of 0.3 mol% of \(1\). As a result, the corresponding cyclic trimers6 are obtained without any detectable by-products such as dimers and teramers (Scheme 2B).

In order to obtain smaller sizes of the hyper-branched star-shaped oligomers for structural analysis, subsequent reduction of the aldehydic end-groups with \(\text{NaBH}_4\) in ethanol was performed, and this generated the corresponding alcohols to prevent further polymerization via aldehyde cyclotrimerization. The oligomers thus obtained were readily soluble in CHCl_3. In a

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particular experiment, a molecular weight of 2,984 and a polydispersity index of 1.47 were obtained from the GPC (THF solvent system with polystyrene standards) analysis for \( 4 \). Based on the solution phase NMR spectroscopic analysis for compounds \( 4, 2,4,6\)-tris(n-Pr)-1,3,5-trioxane (2)\(^8\) and 3-[5-(3-hydroxypropyl)furan-2-yl]propan-1-ol (3),\(^9\) a hyper-branched star-shaped structure can be best described for the composition of the soluble oligomer \( 4 \) (Fig. 1). The solid-state \(^{13}\)C NMR spectrum\(^8\) of the insoluble form obtained from the reaction of furan and acrolin also agreed with the structure prediction based on the solution phase NMR spectrum of compound \( 4 \). According to the differential scanning calorimetric (DSC) analysis of oligomer \( 4 \), two endothermic processes were observed. The first one was peaked sharply at 84.5°C, which was believed to be the glass transition temperature (\( T_g \)). The second one was found broad starting from 105.2°C, which was believed to be the decomposition temperature. A continuing weight loss starting from 104 to 502°C noted on the thermal gravimetric analysis (TGA) curve of oligomer \( 4 \) also coincided with the results obtained from DSC.

In conclusion, we have demonstrated the capability of a single multifunctional organotungsten Lewis acid \( 1 \) in mediating two mechanistically distinct reactions in sequence. The \( 1 \)-catalyzed tandem reactions of F–C/ aldehyde cyclotrimerization have great synthetic application for the formation of star polymers. The hyper-branched star structure and high contents of heterocycles are difficult to generate through conven-
Table 1. 

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*Catalyses were performed in neat substrates. **Conversion is based on the consumption of arene, and the insoluble polymeric products are obtained and analyzed by solid state 13C NMR.*

Scheme 2. (A) I-catalyzed Friedel–Crafts alkylation reactions: compound I: 12 μmol, arene: 12.5 mmol, MVK: 25 mmol, rt, 10 h, 94% isolated yield (X=O); rt, 24 h, 74% isolated yield (X=N); 70°C, 30 h, 96% isolated yield (X=S). (B) 1-catalyzed cyclotrimerization of aldehydes: compound I: 25 μmol, aldehyde: 9.3 mmol, rt, 24 h, 96% isolated yield (R=Me); 93% isolated yield (R=Et); 93% isolated yield (R=n-Pr); 86% isolated yield (R= i-Pr); 88% isolated yield (R=n-Bu).

The scope of the catalytic properties of 1 and the mechanistic implications will be the subject of further investigation.

Acknowledgements

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Figure 1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectra of (a) compound 2, the cyclotrimerization product of butyraldehyde; (b) compound 3, the double Friedel–Crafts alkylation adduct; (c) the furan-based star-shaped oligomer 4. (d) \(^13\)C NMR (100 MHz, CDCl\(_3\)) spectrum of the furan-based star-shaped oligomer 4. * Represents CDCl\(_3\) solvent peak.

References


4. Complexation of crotonaldehyde to a Lewis acid provides a downfield shift of the H atom at C-3 position in the \(^1\)H NMR spectrum and this correlation has been used to compare the relative acid strength of various Lewis acids. See: (a) Childs, R. F.; Mulholland, D. L.; Nixon, A. Can. J. Chem. 1982, 60, 801; (b) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. J. Am. Chem. Soc. 1989, 111, 6070.


7. To a solution of furan (0.4 mL), acrolin (0.74 mL) in CH₂Cl₂ (30 mL) was added 1 (20 mg). The mixture was stirred for 24 h, and was added NaBH₄/EtOH (1 g/10 mL). The reaction was quenched with H₂O after stirring for 4 h. After extraction with CHCl₃ (3×30 mL), the extracts were dried to give 4. Yield: 0.96 g (84%).

8. Compound 1 (20 mg) was added to neat CH₃(CH₂)₂COH (0.84 mL). After stirring for 24 h, CHCl₃ (5 mL) was added before filtration. The filtrate was dried to give white solids 2. Yield: 187 mg (93%).

9. To a solution of furan (0.5 mmol), acrolin (1 mmol) in CH₂Cl₂ (30 mL) was added 1 mL of 2 M H₂SO₄. After 12 h stirring, NaBH₄/EtOH (1 g/10 mL) was added, and the reaction was quenched with H₂O after 5 h stirring. The mixture was extracted with CHCl₃ and washed with hexane to give colorless liquid product 3 after drying. Yield: 0.28 g (28%).

10. The solid-state ¹³C NMR spectrum of the insoluble star-polymers obtained from the reaction of furan and acrolin showed the aldehyde end-group resonance at 204 ppm.