



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

Hsing-Shiun Wang and Shuchun Joyce Yu\*

*Department of Chemistry, National Chung Cheng University, Ming Hsiung, Chia Yi 621, Taiwan*

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**Abstract**—The tris(2-pyridyl)phosphine complex  $[P(2\text{-py})_3W(\text{CO})(\text{NO})_2](\text{BF}_4)_2$  acts as a Lewis acid catalyst precursor for the tandem reactions of Friedel–Crafts/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.<sup>1,2</sup> 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.

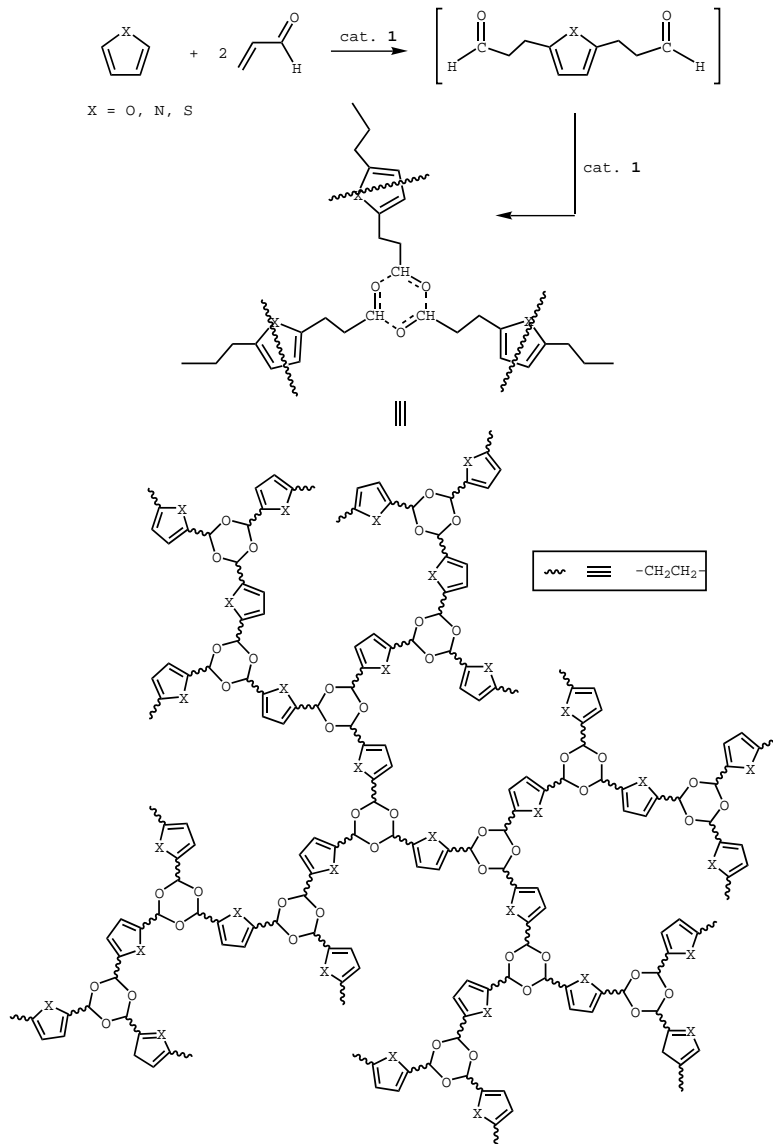
The zero-valent tungsten complex  $[P(2\text{-py})_3W(\text{CO})(\text{NO})_2](\text{BF}_4)_2$  **1**<sup>3</sup> possesses strong Lewis acidity upon loss of the CO ligand, and the relative Lewis acid strength of **1** is found to be comparable to those of  $\text{AlCl}_3$  and  $\text{BF}_3$ .<sup>4</sup> In addition, **1** can be easily prepared in two steps with high yield from  $W(\text{CO})_6$ , 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 acrolin 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,<sup>5</sup> 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  $\text{RCOH}$  ( $\text{R} = \text{Me}, \text{Et}, n\text{-Pr}, i\text{-Pr}, n\text{-Bu}$ ) are used straight without solvents in the presence of 0.3 mol% of **1**. As a result, the corresponding cyclic trimers<sup>6</sup> are obtained without any detectable by-products such as dimers and tetramers (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  $\text{CHCl}_3$ . In a

\* Corresponding author.



















**Scheme 1.** The formation of hyper-branched star polymers catalyzed by  $[P(2\text{-py})_3W(CO)(NO)_2](BF_4)_2$  (**1**).

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**.<sup>7</sup> Based on the solution phase NMR spectroscopic analysis for compounds **4**, 2,4,6-tris(*n*-Pr)-1,3,5-trioxane (**2**)<sup>8</sup> and 3-[5-(3-hydroxypropyl)furan-2-yl]propan-1-ol (**3**),<sup>9</sup> a hyper-branched star-shaped structure can be best described for the composition of the soluble oligomer **4** (Fig. 1). The solid-state <sup>13</sup>C NMR spectrum<sup>10</sup> of the insoluble form obtained from the reaction of furan and acrolein 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

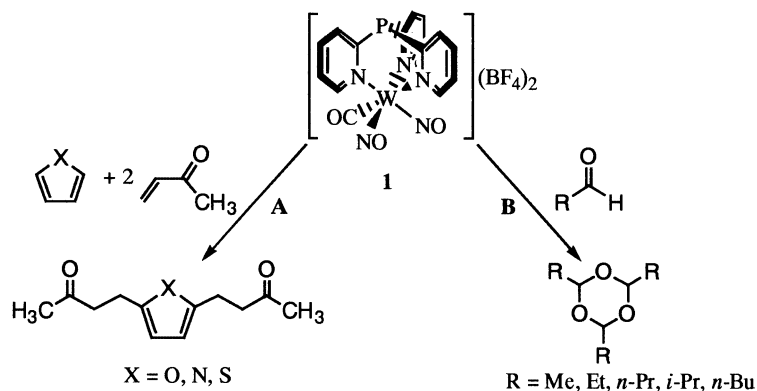
sharply at 84.5°C, which was believed to be the glass transition temperature ( $T_g$ ). The second one was found broad starting from 105.2°C, which was believed to be the decomposition temperature. A continuing weight loss starting from 104 to 502°C noted on the thermal gravimetric analysis (TGA) curve 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.** [P(2-py)<sub>3</sub>W(CO)(NO)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**) catalyzed tandem reactions of Friedel–Crafts/aldehyde cyclotrimerization<sup>a</sup>

Entry	Substrate		Cat. loading [mol%]	T [°C]	t [min]	Conversion [%] <sup>[b]</sup>
	Arene	Enone				
1			1	RT	<1.5	98
2			0.05	RT	30	94
3			1	RT	60	97
4			0.05	RT	120	92
5			1	RT	30	96
6			0.05	RT	60	93
7			1	RT	90	95
8			0.05	RT	150	91

<sup>a</sup>Catalyses were performed in neat substrates. <sup>b</sup>% Conversion is based on the consumption of arene, and the insoluble polymeric products are obtained and analyzed by solid state <sup>13</sup>C NMR.



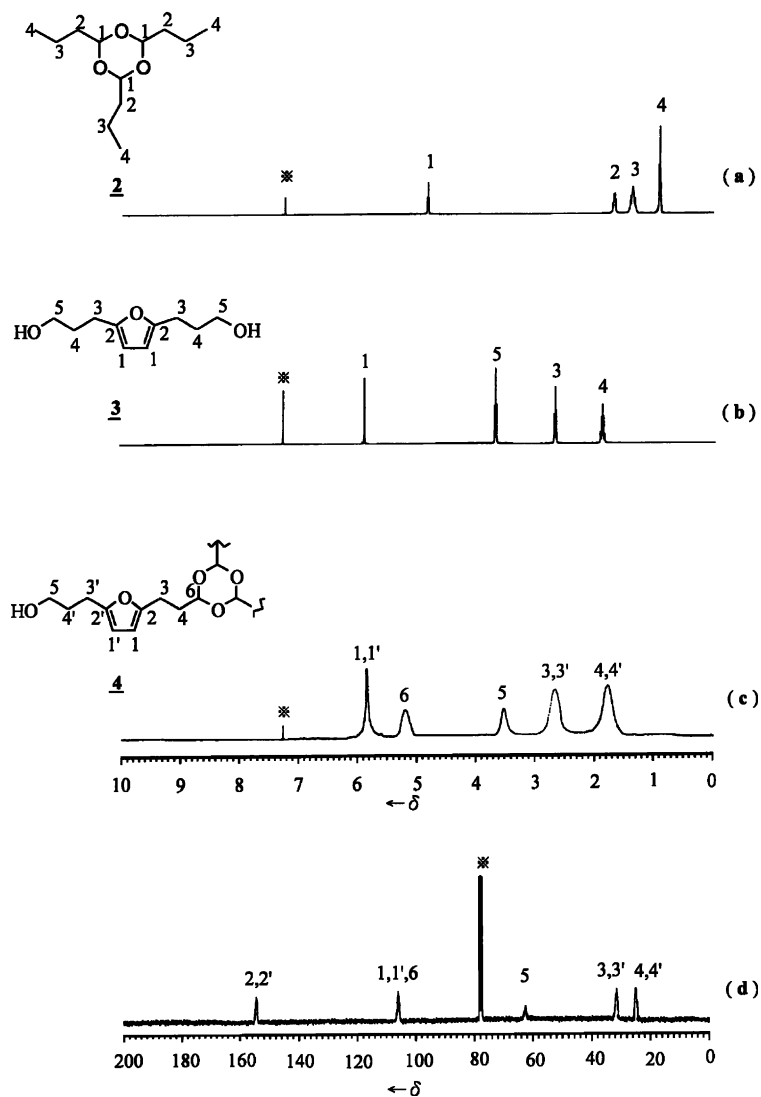
**Scheme 2.** (A) **1**-catalyzed Friedel–Crafts alkylation reactions: compound **1**: 12 μmol, arene: 12.5 mmol, MVK: 25 mmol, rt, 10 h, 94% isolated yield (X=O); rt, 24 h, 74% isolated yield (X=N); 70°C, 30 h, 96% isolated yield (X=S). (B) **1**-catalyzed cyclotrimerization of aldehydes: compound **1**: 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).

tional synthetic methods, and they are believed to be important elements for high-temperature polymers.<sup>11</sup>

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.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 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)  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of the furan-based star-shaped oligomer **4**. \* Represents  $\text{CDCl}_3$  solvent peak.

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7. To a solution of furan (0.4 mL), acrolin (0.74 mL) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added **1** (20 mg). The mixture was stirred for 24 h, and was added NaBH<sub>4</sub>/EtOH (1 g/10 mL). The reaction was quenched with H<sub>2</sub>O after stirring for 4 h. After extraction with CHCl<sub>3</sub> (3×30 mL), the extracts were dried to give **4**. Yield: 0.96 g (84%).
8. Compound **1** (20 mg) was added to neat CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>COH (0.84 mL). After stirring for 24 h, CHCl<sub>3</sub> (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 CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added 1 mL of 2 M H<sub>2</sub>SO<sub>4</sub>. After 12 h stirring, NaBH<sub>4</sub>/EtOH (1 g/10 mL) was added, and the reaction was quenched with H<sub>2</sub>O after 5 h stirring. The mixture was extracted with CHCl<sub>3</sub> and washed with hexane to give colorless liquid product **3** after drying. Yield: 0.28 g (28%).
10. The solid-state <sup>13</sup>C NMR spectrum of the insoluble star-polymers obtained from the reaction of furan and acrolin showed the aldehydic end-group resonance at 204 ppm.
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