



Recoverable platinum bis(fluoro-ponytailed) bipyridine complex as catalyst for hydrosilylation of alkynes under thermomorphic condition



Norman Lu^{a,*}, Wei-Cheng Chung^a, Hsing-Fang Chiang^a, Yung-Cheng Fang^a,
Ling-Kang Liu^{a,b}

^a Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei 106, Taiwan

^b Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

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ABSTRACT

The fluorous PtCl₂[5,5'-bis-(n-C₁₁F₂₃CH₂OCH₂)-2,2'-bpy] complex (**2**) was prepared and employed as recoverable catalyst for the hydrosilylation of alkynes. Pt-catalyst **2** with F-content 0.53 was recovered under the thermomorphic method by design and the catalyst was demonstrated capable of re-usage for 8 times without loss of activity. The leaching of Pt in product mixture was monitored, with ICP-MS, to be at as low as 10⁻⁶ level per cycle in the 5-decyne reactions and at 10⁻³ level per cycle in the (HO)CMe₂C≡CH reaction. The reaction-catalyst fulfills the principle of green chemistry, and with its addition nature the hydrosilylation delivers 100% atom economy. The easily prepared polyfluorinated (2,2'-bpy)Pt complex **2** is the robust and thermally stable catalyst, which doesn't require specific handling for utilization and storage in laboratory.

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1. Introduction

Although homogeneous catalysis is a powerful tool in highly active and stereoselective organic transformations,¹ the majority of catalytic processes in industry are still conducted under heterogeneous conditions, because the separation of the catalysts from the product mixture is easier than under homogeneous conditions. Thus besides developing homogeneous catalysts that can be used in very low concentrations (for which the catalyst quantity is below the ppm level), efforts have been made to provide heterogeneous reactions, which need the catalysts to be fixed to a solid support.^{2,3} In other words, it is important to find a recoverable catalyst to be easily separated from the product mixture after reaction.⁴

One of the new approaches to solve the problems of separation and catalytic efficiency is the thermomorphic catalysis^{2,3,5,6} with or without the fluororous solvents. Bergbreiter et al. used a polymer-based thermomorphic system whose polymeric support was not totally dissolved at high temperature.^{2,3} Gladysz et al. published the results of fluorinated compounds to catalyze addition reaction on

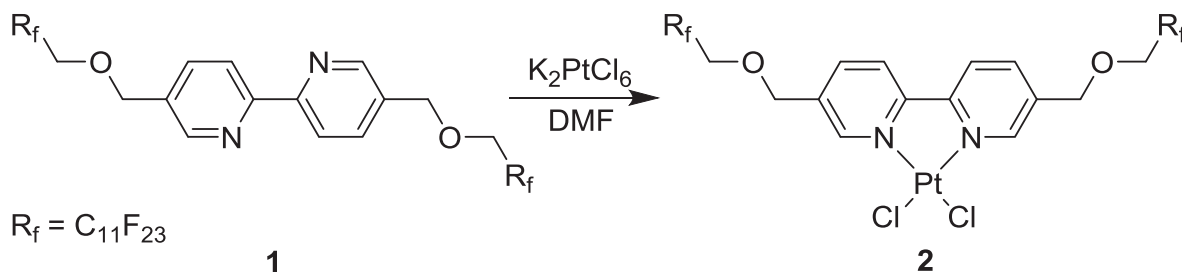
unsaturated substrates without the use of expensive fluororous solvents.^{5,6} Fan et al. demonstrated the use of the thermomorphic system with a non-fluorous catalyst for asymmetric hydrogenation.⁷ Yamamoto et al. prepared recyclable fluororous catalysts by using liquid/solid phase separation without fluororous solvents.^{8,9} Progress in our laboratory was mainly a recyclable polyfluorinated bipyridine metal complex system in the application on cross-coupling C–C bond formation reactions.¹⁰

Recovery and reuse with fluororous catalysts may have its strength if compared to that with the non-fluorous ones, because additional fluororous interactions could be utilized as controlling tool. A unique feature in ideal thermomorphic catalysis is that the reaction mixture is homogeneous at high temperature during reaction and the product mixture becomes phase separated when being cooled after reaction, taking advantages of the thermomorphic property of compounds carrying high fluorine content.^{11,12}

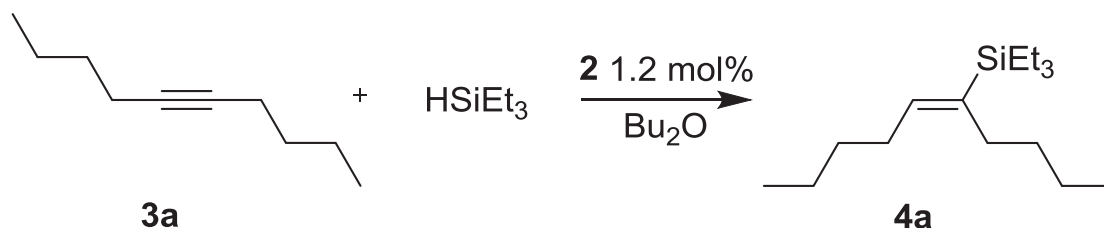
The high price of platinum raw material makes recovery of platinum-catalysts more valuable, on top of its homogeneous catalysis that offers advantages such as high efficiency, better tuning of chemoselectivity, regioselectivity and/or stereoselectivity. Ramon et al. used impregnated Pt on magnetite as the recyclable catalyst for the hydrosilylation of alkynes.¹³ The hydrosilylation of alkynes produces olefinic silanes that are potential precursors of trisubstituted alkenes, i.e., the resulting organosilicon reagents are

* Corresponding author. Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei 106, Taiwan.

E-mail address: normanlu@mail.ntut.edu.tw (N. Lu).



Scheme 1.



Scheme 2.

versatile building blocks in a number of synthetic processes. The transition metal-catalyzed hydrosilylation of alkynes represents the most straightforward and convenient route for the preparation of olefinic silanes with 100% atom efficiency.¹⁴ In this research, we selected for demonstration the Pt-catalyzed reactions on hydrosilylation of alkyne using specifically a dichloro Pt-diimine complex that carries long fluorinated-ponytails at periphery of 2,2'-bpy for recycling studies. Such Pt complexes are known to be soluble in organic solvent only at elevated temperatures, e. g. in Bu₂O, yet insoluble at all at room temperature. The use of expensive fluorinated solvents is thus avoided, the homogeneous catalysis achieved, and the Pt-catalysts recovered and reused using a simple procedure. To our knowledge, this is the first time Pt-catalyzed hydrosilylation of alkynes has been successfully tested for the feasibility of recycling usage under the thermomorphic conditions.

2. Results and discussion

2.1. Catalyst synthesis

The preparation of ligand bis-5,5'-(*n*-C₁₁F₂₃CH₂OCH₂)-2,2'-bpy (**1**) followed a literature procedure.¹⁵ The ligand has a high fluorine content, F% = 0.64. The reaction of fluorinated bipyridine ligand **1** with K₂PtCl₄ in DMF, as shown in Scheme 1, resulted in the Pt complex PtCl₂[5,5'-bis-(*n*-C₁₁F₂₃CH₂OCH₂)-2,2'-bpy] (**2**) as red solids. Compound **2** exhibits a fluorine content at F% = 0.53 and has a slight solubility in Bu₂O at 120 °C. The color of solution becomes red. Compound **2** is insoluble in Bu₂O at 25 °C, however.

2.2. General procedure for recovery and reuse of **2** in hydrosilylation reaction

The Pt complex **2** was then tested for the subsequent catalytic experiments to examine the addition of HSiEt₃ to (a) symmetrical internal alkyne 5-decyne (**3a**), (b) terminal alkyne 1-hexyne (**3b**), and (c) functionalized terminal propargylic alkyne (**3c**), in the hydrosilylation reactions.¹⁶

The Pt-catalyzed hydrosilylation reactions of **3a-c** with HSiEt₃ were carried out that successfully demonstrated the feasibility of recycling usage with **2** as the catalyst using Bu₂O as the solvent

under the thermomorphic condition. The catalytic reaction was conducted at ca 120 °C for about 4 h in each run. At the end of each cycle, the product mixtures were cooled to room temperature then centrifuged for precipitation of the Pt catalyst **2**. After the Pt catalyst was recovered by decantation, the collected **2** was again supplied with the same amounts of Bu₂O solvent, **3a-c**, and HSiEt₃ to proceed to the next cycle. The products were quantified with GC/MS and ¹H NMR analysis, using NMP as internal standard.

2.3. Recovery and reuse of **2** in hydrosilylation reaction of 5-decyne

Product analysis of the hydrosilylation reaction indicated only one product of [(*E*)-dec-5-en-5-yl]triethylsilane (**4a**), in quantitative yields, as shown in Scheme 2, with the (*Z*)-form isomer unobserved. Thus it became a good model reaction to study the recovery and reuse of polyfluorinated Pt-catalyst **2**, using **3a** and HSiEt₃ in the hydrosilylation reaction. The products were quantified with GC/MS and ¹H NMR analysis, using NMP as internal standard. Very good recycling results (Table 1), for a total of 8 times were achieved for Pt-catalyst **2**-catalyzed hydrosilylation without difficulty under the thermomorphic mode.

Ramon et al. studied the hydrosilylation reaction with recyclable PtO/PtO₂-Fe₃O₄ catalyst in the absence of any solvent on **3a** and HSiEt₃ and yielded just **4a** quantitatively.¹³ Shafir and Pleixats et al. studied tris-imidazolium salt-stabilized Pd nanoparticles and

Table 1
Recycling results of **2**-catalyzed hydrosilylation reaction of symmetrical internal alkyne R–≡–R.^a

Cycle no.	Reactant (R=)	Time (h)	Temp (°C)	Yield ^(b) (%)	TON
1	n-Bu	4	120	>97	80.8
2	n-Bu	4	120	>97	80.8
3	n-Bu	4	120	>97	80.8
4	n-Bu	4	120	>97	80.8
5	n-Bu	4	120	>97	80.8
6	n-Bu	4	120	>97	80.8
7	n-Bu	4	120	>97	80.8
8	n-Bu	4	120	>97	80.8

^a Reaction conditions: Bu₂O as solvent (2 mL), 5-decyne **3a** (1.55 mmol, 214 mg), HSiEt₃ (2 mmol, 233 mg), 1.2 mol % Pt catalyst **2** (0.0186 mmol; 30.6 mg).

^b Yields mainly determined by ¹H NMR area integration on product solution.

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