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Graphic Abstract

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Recoverable Platinum Bis(fluoro-ponytailed) Bipyridine Complex as Catalyst for Hydrosilylation of Alkynes Under Thermomorphic Condition

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Abstract

The fluorous $PtCl_2[5,5'-bis-(n-C_{11}F_{23}CH_2OCH_2)-2,2'-bpy]$ 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.

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 fluorous 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 fluorous 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 fluorous catalysts by using liquid/solid phase separation without fluorous 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 fluorous catalysts may have its strength if compared to that with the non-fluorous ones, because additional fluorous 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 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 fluorous-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.

Results and discussion

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

 $PtCl_2[5,5'-bis-(n-C_{11}F_{23}CH_2OCH_2)-2,2'-bpy]$ (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. 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 $HSiEt_3$ 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.

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



Scheme 2

Product analysis of the hydrosilylation reaction indicated only one product of [(5E)-dec-5-en-5-yl]triethylsilane (4a), in quantitative yields, as shown in Scheme 2, with the (5Z)-form isomer

un-observed. 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.

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

Table 1. Recycling results of 2-catalyzed hydrosilylation reaction of symmetrical internal alkyne $R = -R^a$

^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.

Ramón *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 reported the hydrosilylation of **3a** with HSiEt₃ resulted also in only **4a**, at 60% yield with a different recyclable metal.¹⁷ In this manuscript, the **2**-catalyzed hydrosilylation reaction of **3a** with HSiEt₃ resulted in also one product **4a** quantitatively.

4. Recovery and reuse of 2 in hydrosilylation reaction of 1-hexyne



In the second Pt-catalyzed hydrosilylation reaction for simple terminal 1-hexyne (**3b**), the ¹H NMR spectrum of hydrosilylation product mixtures clearly indicated two products (*E*)-triethyl(hex-1-en-1-yl)silane (**4b**) and triethyl(hex-1-en-2-yl)silane (**5b**) as shown in Scheme 3. In Table 2 the hydrosilylation reaction of **3b** with HSiEt₃ catalyzed by **2** showed very good recycling results for a total of 8 times. The two isomeric products were obtained with >97% total yield all the time.

Cycle No.	Reactant (R ₁ =)	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	98	81.7
6	n-Bu	4	120	>97	80.8
7	n-Bu	4	120	>97	80.8
8	n-Bu	4	120	>97	80.8

Table 2. Recycling results of 2-catalyzed hydrosilylation reaction of terminal $R_1 = -H^a$

^a Reaction conditions: Bu₂O (2mL) as solvent, 1-hexyne **3b** (1.52 mmol, 125 mg), HSiEt₃ (1.92 mmol, 223 mg), 1.2 mol % Pt catalyst **2** (0.0186 mmol, 30 mg). ^b Yields determined by ¹H NMR area integration on product solution.

Figure 1 details the ¹H NMR spectrum of the product mixture for the **3b** reaction, focusing on the double bond proton region, which indicates clearly the presence of **4b** and **5b** without the presence of third isomer (*Z*)-triethyl(hex-1-en-1-yl)silane, nonetheless. The ¹H NMR spectrum of **4b** shows the alkenyl protons at δ 5.96 (dt, *J* = 18.6, 6.2 Hz, 1 H), 5.46 (dt, *J* = 18.6, 1.2 Hz, 1 H) with typical coupling constant of 18.6 Hz for the alkenyl protons at *trans* positions; that of **5b**

shows the alkenyl protons at δ 5.55 (dt, J = 3.1, 1.5 Hz, 1 H), 5.20 (dt, J = 3.1, 0.6 Hz, 1 H) with typical coupling constant of 3.1 Hz for the germinal ones. Concerning the (*Z*)-triethyl(hex-1-en-1-yl)silane isomer, a coupling constant of 6-12 Hz is expected, yet not seen, in Figure 1.



Figure 1. ¹H-NMR spectrum (CDCl₃, δ 5.0-6.1) of the product mixtures from Scheme 3.

The GC/MS method was employed to look into the products. After stirring for 4 h, the product mixtures were analyzed (see Figure 2). The GC peaks at retention times of 3.2 min and 6.0 min are the signals for reagent (HSiEt₃, slight excess) and high boiling solvent (Bu₂O), respectively. The peak at retention time of 1.8 min for **3b** disappeared and two new peaks at retention times of about 12.0 and 12.3 min appeared, which were subject to MS identification (Figure 2b-c). Both mass spectra of species at 12.0 min and 12.3 min showed weak peak at m/e = 198 [M⁺] and major fragmentation peaks at m/e = 169 [M⁺-Et] and 141 [M⁺-Bu], in different ratios. The MS results clearly demonstrated that only two isomeric products resulted from the Pt-catalyzed hydrosilylation of terminal 1-hexyne. The ratio of peak area integrations by GC is 56:44, consistent to the ¹H NMR area integration ratio of the two products **4b** and **5b**, 1:0.84.





The Tsipis' PtCl₂-catalyzed version of **3b** with HSiEt₃ yielded **4b** and **5b** (96:4, 93% total yield). Tsipis had noted that the magnitude of difference in ¹³C chemical shifts for terminal alkynes is rather large (~15–20 δ units) compared to that for internal alkynes (~3–5 δ units).¹⁸ In our study, the **2**-catalyzed hydrosilylation of 1-hexyne **3b** with HSiEt₃ resulted in **4b** and **5b** (56:44, >97% total yield). A diminishing regioselectivity was observed in current study, likely because the coordination sphere of (2,2'-bpy)PtCl₂ remains largely unaltered, which might have caused enough electronic difference from that of a loose coordination sphere of PtCl₂.

5. Recovery and reuse of 2 in hydrosilylation reaction of 2-methylbut-3-yn-2-ol

In the third Pt-catalyzed hydrosilylation reaction (Scheme 4), for more complicated terminal alkyne (HO)CMe₂C \equiv CH (**3c**) with HSiEt₃, the propargyl alkyne **3c** has a hydroxyl group as well as a sterically crowded C-atom next to the triple bond. The recycling experiments using Pt-catalyst **2** proceeded without difficulty for 8 times (Table 3), giving yields > 97 % for total isomeric products.



The Pt-catalyzed hydrosilylation of **3c** with HSiEt₃ was noticed that reactivity was seemingly less than that of 1-hexyne **3b** with HSiEt₃, although the rates were not strictly measured in this study. The reaction was monitored with GC/MS and ¹H NMR. Figure 3 shows a typical gas chromatogram of the product mixtures after catalysis. No peak could be attributed to the starting 3c (if present, it should be located at retention time 1.8 min). The HSiEt₃ peak (slight excess in reaction) was observed at retention time 3.2 min and the Bu₂O peak (solvent) was observed at retention time 5.9 min. Two new peaks were recorded at 12.3 and 12.5 min, which were assigned to the products (see later for ¹H NMR analysis).

Cycle No.	Reactant ($R_2 =$)	Time (h)	Temp (°C)	Yield ^[b] (%)	TON
1	HOC(Me) ₂	4	120	>97	80.8
2	HOC(Me) ₂	4	120	>97	80.8
3	HOC(Me) ₂	4	120	>97	80.8
4	HOC(Me) ₂	4	120	>97	80.8
5	HOC(Me) ₂	4	120	>.97	80.8
6	HOC(Me) ₂	4	120	>97	80.8
7	HOC(Me) ₂	4	120	>97	80.8
8	HOC(Me) ₂	4	120	>97	80.8

Table 3. Recycling results of 2-catalyzed hydrosilylation reaction of terminal R₂-=-H

^a Reaction conditions: Bu₂O (2 mL) as solvent, 2-methylbut-3-yn-2-ol **3c** (1.52 mmol, 128 mg), HSiEt₃ (1.92 mmol, 223 mg), 1.2 mol% Pt catalyst 2 (0.0186 mmol, 30 mg). ^b Yields determined by ¹H NMR area integration on product solution.

The HSiEt₃ addition to (HO)CMe₂C=CH **3c** would generate three possible product isomers, all with molecular mass of 200. The two isolated products were found to be (*E*)-2-methyl-4-(triethylsilyl)but-3-en-2-ol **4c** with retention time of 12.3 min and 2-methyl-3-(triethylsilyl)but-3-en-2-ol **5c** with retention time of 12.5 min. The ratio from area integration for **4c** to **5c** in the gas



Figure 3. The GC/MS results for the products in Scheme 4. (a) the GC chromatogram, with (b) the MS data for peak at retention time 12.3 min (**4c**) and (c) that at 12.5 min (**5c**).

chromatogram was about 67:33. For 4c the MS data indicated only a small signal for M^+ (m/e= 200) but intense signal for M⁺-Et (m/e= 171). For 5c the MS data showed even less intensity for both M^+ (m/e=200)and M^+ –Et (m/e=171) The possible peaks. (Z)-2-methyl-4-(triethylsilyl)but-3-en-2-ol isomer was not detected in GC/MS. Besides catalyst 2, another catalyst, $PtCl_2[5,5'-bis-(n-C_9F_{19}CH_2OCH_2)-2,2'-bpy]$ (2'), was also used to test the different fluorous ponytailed Pt-catalyzed hydrosilylation reaction of 2-methylbut-3-yn-2-ol. The results also gave a mixture of two hydrosilylated isomers with about the same ratio.

The ¹H NMR spectrum of the product solution is shown in Figure 4. There are two sets of peaks in the C=C double bond region. One set of olefinic protons shows signals at δ 6.11 (d, J = 19 Hz, 1H), δ 5.70 (d, J = 19 Hz, 1H), assigned to the *trans* positioned protons of **4c**. The second set of vinyl protons are at δ 5.69 and 5.24 with J = 1.8Hz, assigned to germinal protons of **5c**. The peak area integration ratio between **4c** and **5c** is approximately 2:1, similar to the GC area integration ratio.



Figure 4. ¹H-NMR of product solution of Scheme 4 (CDCl₃, δ 5.1-6.2).

Cook *et al.* found that the hydrosilylation of **3c** and HSiEt₃ using PtCl₂ and XPhos ligand limited the products to just **4c** (89% yield) as a colorless oil.¹⁹ In early Russian literatures, **3c** and HSiEt₃ catalyzed by H₂PtCl₆ gave **4c** and **5c** with no reported ratio.²⁰ The impregnated Pt on magnetite PtO/PtO₂-Fe₃O₄ recyclable catalyst used by Ramón *et al.* in the hydrosilylation of **3c** with HSiEt₃ (neat) gave **4c** and **5c** (78:22, 99% total yield).¹³ Tsipis in his PtCl₂ catalyzed hydrosilylation reaction of **3c** produced **4c** 93% and **5c** 7% (88% total yield).¹⁹ The similar HSiEt₃ addition to **3c** in this study produced **4c** and **5c** (67:33, > 97% total yield). The propargylic alcohol functional group may have influence in addition to steric and electronic effects (*vide infra*).

6. Analysis of residual Pt level in product solution by ICP-MS

As solid the Pt-catalyst **2** was separated from the reaction mixtures after centrifugation. The recovered catalyst **2** was then ready for reuse in the next cycle of hydrosilylation reaction. The quantity of residual Pt metal present in the solution was also analyzed, taking random samples among the product solutions resulting from the thermomorphic hydrosilylation process. The polyfluorinated (2,2'-bpy)PtCl₂ complexes are robust. Only very low Pt leaching was observed in solution from the complex **2** after the thermomorphic, homogeneous catalysis procedure (Table 4). The first three entries of Table 4 (1–1, 1–3, 1–6) are samples taken from product mixtures after cycles 1, 3, and 6 of the hydrosilylation of **3a**, and the Pt leaching levels by ICP-MS are 6.7×10^{-5} , 6.1×10^{-5} , and 1.6×10^{-5} , respectively, averaging at 5.5×10^{-5} . It provided strong evidence that the molecular catalyst **2** studied in this research possesses great thermostability and is indeed a robust, reliable and recoverable Pt catalyst under the thermomorphic conditions. In the bottom entries of Table 4 (3–2, 3–4), the hydrosilylation of (HO)CMe₂C=CH **3c** exhibits a greater Pt leaching level in the range of $1.4 \cdot 1.5 \times 10^{-3}$. The increase of the Pt leaching level for the

hydrosilylation of **3c** could be attributed to the tertiary propargyl –OH functionality as an extra site for coordination to the Pt metal ion center during the catalytic cycle. There is no such –OH functionality in **3a** and **3b**.

	6		
Table no.–Run no. ^a	Pt (in ppb)	Leaching level ^b	Recovery (%)
	Detected from ICP-MS		
1-1	60.8	3.35×10^{-5}	99.997
1–3	55.6	3.05×10 ⁻⁵	99.997
1-6	15.9	8×10 ⁻⁶	99.999
2-2	87.8	4.85×10 ⁻⁵	99.995
2-4	69.3	3.80×10 ⁻⁵	99.996
2-7	36.1	2.00×10 ⁻⁵	99.998
3–2	2630	0.75×10 ⁻³	99.925
3-4	2570	0.70×10^{-3}	99.930

Table 4. The ICP-MS results of Pt leaching levels

^a For example, 1–1 stands for the entry 1 from Table 1. ^bThe Pt leaching level is calculated as follows, using entry 1–1 as example: $(60.8 \text{ ppb} \times 2 \text{ mL}) / (0.0186 \text{ mmol Pt}) = 60.8 \times (\text{mgPt}/10^{3}\text{L}) \times 2 \times (10^{-3}\text{L}) / (1.86 \times 10^{-2} \times 195 \text{ mgPt}) = 3.35 \times 10^{-5}$.

In literature, the recyclable impregnated Pt on magnetite PtO/PtO_2 -Fe₃O₄ catalyst by Ramón *et al.* in the hydrosilylation reaction had been reported about the Pt leaching level, at 0.01% of the initial amount of Pt (ICP-MS analysis of the resulting product mixture, and 0.0008% reportedly for Fe).¹³ Thus, the recycling Pt catalyst **2** performs really great with the lowest leaching level of only 0.001% (entry 1-6) while utilizing the thermomorphic method.

7. Mechanistic insights

Overall, the hydrosilylation with Pt complex 2 is believed to follow the Chalk–Harrod mechanism. The Et₃SiH is oxidatively added to [Pt], followed by coordination of the alkyne and insertion to [Pt]–H bond. The reductive elimination results in the *cis* addition of Si–H onto an alkyne triple bond,¹⁶ as shown in Scheme 5. The electronic effect that the polarization of an alkyne in hydrosilylation reaction would direct the hydride addition to the more electropositive C-atom, was first summarized by Tsipis in a PtCl₂ catalyzed hydrosilylation.¹⁹ This electronic effect leaves the steric C-atom directing force only a secondary factor to affect regioselectivity.



Scheme 5. Electronic influence on Pt-catalyzed hydrosilylation.

At the molecular level, the coordination sphere of **2** with a (2,2'-bpy)PtCl₂ core remains largely unaltered, which might have caused enough electronic difference from that of a loose coordination sphere of PtCl₂. Concerning the propargylic alcohol **3c**, Ferreira *et al.* had analyzed the influences dictating regioselectivity in Pt-catalyzed hydrosilylation reactions of internal alkynes,^{21,22} and suggested that the impact of the propargylic alcohol functional group on hydrosilylation regioselectivity cannot be fully explained with simple steric and electronic arguments, and had hypothesized that the –OH functional group is participating in an interaction with the Pt catalytic complex, perhaps through hydrogen bonding.

As a summary, we have demonstrated, to our knowledge, the first example of Pt-catalyzed hydrosilylation reaction of symmetric internal alkyne and terminal alkynes under the thermomorphic conditions, all being with good turnover numbers on hydrosilylation catalysis and easy recovery and re-usage for 8 cycles without loss of reactivity. The preparation of fluorous $PtCl_2[5,5'-bis-(n-C_{11}F_{23}CH_2OCH_2)-2,2'-bpy]$ catalyst was simple, with built-in molecular designs. The leaching level of Pt in the product mixture was only as low as 0.001%.

8. Experimental section

8.1. General procedures

Gas chromatographic/mass spectrometric data were obtained using an Agilent 6890 Series gas chromatograph with a series 5973 mass selective detector. The reaction was monitored with a HP 6890 GC using a 30 m 0.250 mm HP-1 capillary column with a 0.25 µm stationary phase film thickness. The flow rate was 1 mL/min and splitless. Samples analyzed by fast atom bombardment (FAB) mass spectroscopy were done by the staff of the National Central University (Taiwan) mass spectrometry laboratory. The amounts of residual Pt samples were analyzed by ICP-MS. Infra-red spectra were obtained on a Perkin–Elmer RX I FT-IR Spectrometer. NMR

spectra were recorded on Bruker AM 500 and Joel AM 200 using 5 mm sample tubes. CD₃OD, CD₂Cl₂, CDCl₃, deuterated DMF and deuterated Me₂SO were the references for both ¹H and ¹³C NMR spectra; and Freon® 11 (CFCl₃) was the reference for ¹⁹F NMR spectra.

8.1.1. Starting materials

Chemicals, reagents, and solvents employed were commercially available and used as received. $C_{11}F_{23}CH_2OH$ were purchased from Aldrich and SynQuest.

8.2. Preparation of Pt complex 2

The reaction of K_2PtCl_4 with fluorinated bipyridine derivatives, 5,5'-bis $(n-C_{11}F_{23}CH_2OCH_2)-2,2'$ -bpy (1), resulted in $PtCl_2[5,5'$ -bis- $(n-C_{11}F_{23}CH_2OCH_2)-2,2'$ -bpy] (2), as red solids. The reaction was stirred under nitrogen for 4 h, and the complex 2 would then precipitate from the reaction mixture. After collection of the precipitates, water and Et₂O were used to wash the red solids for several times, and the yield was 87%.

8.2.1. Analytical data of 2

¹H NMR (500 MHz, DMF- d_6 , at 90 °C, δ ppm, *J* Hz; very weak sample): 8.72 (d, 2H, H6), 8.48 (s, 2H, H3), 7.32 (d, 2H, H5) , 4.88 (4H, s, bpy-CH₂), 4.12 (t, 4H, C₁₁F₂₃-CH₂); ¹⁹F NMR (470.5 MHz, DMF- d_6 , δ ppm, *J* Hz; very weak sample) -81.7 (t, 6F, -CF₃), 119.3 ~125.7 (broad peaks, 20 F, -C₁₀F₂₀); ¹³C NMR spectrum was not obtained due to the extremely weak signals at 90 °C. FT-IR: 1601, 1559 (v_{bpy}, w), 1197, 1148 (C–F stretch, s).

HR-MS (FAB):

 $[M^{+}] C_{36}H_{14}{}^{35}Cl_{2}F_{46}N_{2}O_{2}Pt \ \textit{m/e} \ calc: 1644.9346, \ found: 1644.9327; \ C_{36}H_{14}{}^{35}Cl^{37}ClF_{46}N_{2}O_{2}Pt \ \textit{m/e} \ calc: 1646.9328, \ found: 1646.9321; \ C_{36}H_{14}{}^{37}Cl_{2}F_{46}N_{2}O_{2}Pt \ \textit{m/e} \ calc: 1648.9287, \ found: 1648.9280.$

8.3. Recycling studies

A tube was charged with Bu_2O (2 mL) as solvent, alkyne substrate (1.52 mmol), HSiEt₃ (1.92 mmol, 223 mg), and 1.2 mol% Pt catalyst **2** (0.0186 mmol, 30 mg) for heating to 120 °C and then maintained stirring at 120 °C under N₂ atmosphere. During the reaction the reaction mixture became colored (Figure 5b) and the mixture was periodically monitored by GC/MS for completion. After 4h, the temperature was lowered to 25 °C, followed by centrifugation to precipitate the Pt catalyst **2** (Figure 5c). The product mixtures were withdrawn using a syringe for analysis. The Pt catalyst **2** was rinsed with Bu_2O for 3 times before next charging of the solvent and reactants for catalytic study. Total number of recycling is 8 times.

Over the time, the Pt-catalyzed hydrosilylation reaction products were also isolated for characterization. Since the products (**4a**, **4b**, **4c**, **5b**, and **5c**) were known, they showed correct GC/MS and ¹H NMR data, and m.p. for solids.^{13,19,20,23}



Figure 5. (a) Graphic representation of Pt catalyst recycle under thermomorphic condition; (b) The colored reaction mixtures during hydrosilylation reaction; (c) The product mixture separated from Pt catalyst **2** after centrifugation.

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Supplementary data

Supplementary material which is associated with this article to show the pictures of the process in recovering the catalyst can be found in the online version, at

References and notes

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Highlights

- Pt-catalyst 2 with F-content 0.53 was easily recoverable under the thermomorphic method.
- Pt complex 2 is the robust and thermally stable catalyst.
- The leaching of Pt was monitored by ICP-MS to be as low as 10^{-6} level per cycle.
- The reaction-catalyst fulfills the principle of green chemistry, and the hydrosilylation delivers 100% atom economy.