

# Convenient synthesis of Pt(0) olefin complexes by colorimetric reduction of Pt(II) complexes with SmI<sub>2</sub>

Sensuke Ogoshi<sup>\*</sup>, Masaki Morita, Katsuharu Inoue, Hideo Kurosawa<sup>\*</sup>

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

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## Abstract

Homoleptic olefin platinum(0) complexes, Pt(C<sub>7</sub>H<sub>10</sub>)<sub>3</sub> and Pt(cod)<sub>2</sub>, were synthesized by the colorimetric reduction of platinum(II) complexes with SmI<sub>2</sub> in the presence of 2-norbornene or COD. This is a practically more convenient method for the synthesis of the Pt(0) complexes than the literature method employing Li<sub>2</sub>(cot).

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**Keywords:** SmI<sub>2</sub>; Colorimetric reduction; Homoleptic olefin platinum(0) complexes

## 1. Introduction

Zerovalent group 10 transition metal complexes, especially homoleptic olefin complexes, are very useful as a catalyst precursor in organic transformation reactions and as a starting material in the synthesis of organometallic compounds. For example, Ni(cod)<sub>2</sub>, which is commercially available, is employed as a catalyst precursor frequently. On the other hand, commercially unavailable platinum(0) olefin complexes have to be prepared prior to use. So far, Li<sub>2</sub>(cot) has been employed as a reductant in the reduction of platinum(II) to platinum(0) complex in the presence of olefins [1]. However, Li<sub>2</sub>(cot) is inconvenient for use due to its instability, difficulty to store and necessity to measure the concentration in advance. Therefore, practically more convenient reductants are desired (recently, the convenient synthesis of tris(styrene)platinum(0) complex, which cannot be isolated as a solid, by reduction of *cis*-PtCl<sub>2</sub>(PhCH=CH<sub>2</sub>)<sub>2</sub> with triphenylsilane has been reported, see [2]).

SmI<sub>2</sub> is a very useful, convenient and mild one electron reducing reagent, which is much easier to prepare and handle than Li<sub>2</sub>(cot). Especially, SmI<sub>2</sub> appears to have a greater advantage than Li<sub>2</sub>(cot) in that it is commercially available and there is the color change

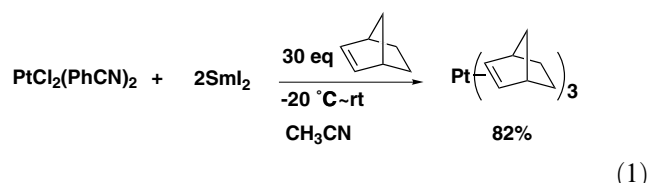
from purple (Sm(II)) to yellow (Sm(III)). The latter characteristic feature would allow us to judge the end point of the reaction without difficulty. Reductive transformations of organic compounds with SmI<sub>2</sub> have been reported (recent reviews on SmI<sub>2</sub>-mediated organic transformations, see [3]). In the presence of catalytic amount of palladium complex, SmI<sub>2</sub> was employed as a reductant to convert electrophilic substrate to a nucleophilic intermediate [4]. With regard to application of SmI<sub>2</sub> to the synthesis of organometallic complexes, preparation of Ti(III) complex by reduction of Ti(IV) complex with SmI<sub>2</sub> (reaction of transition metal center, see [5]) and reductive transformation of functional groups of organic ligands in a few late transition metal complexes with SmI<sub>2</sub> have been reported (transformations of organic functionalities in transition metal complexes, see [6]). However, there are no reports on the use of SmI<sub>2</sub> in the synthesis of organometallic compounds of late transition metals by direct reduction of the metals in the starting materials. Here, we report a convenient method to prepare platinum(0) olefin complexes by the reduction of Pt(II) complexes with SmI<sub>2</sub>.

## 2. Results and discussion

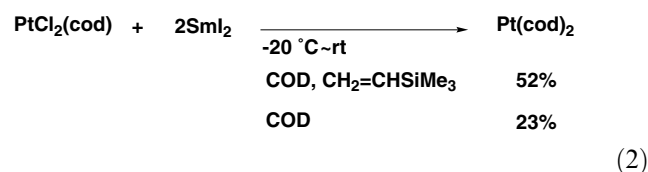
In the presence of norbornene (30 eq), SmI<sub>2</sub> (0.1 M, CH<sub>3</sub>CN solution) was added to a suspension of PtCl<sub>2</sub>(PhCN)<sub>2</sub> in CH<sub>3</sub>CN dropwise at –20 °C until the color did

<sup>\*</sup> Corresponding authors. Tel.: +81668797393; fax: +81668797394.  
E-mail address: [kurosawa@chem.eng.osaka-u.ac.jp](mailto:kurosawa@chem.eng.osaka-u.ac.jp) (H. Kurosawa).

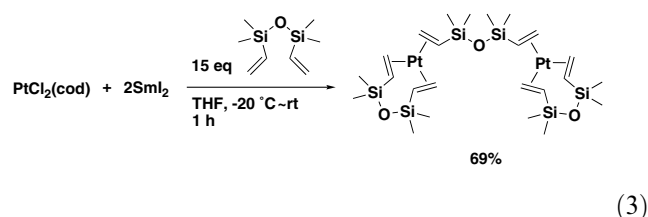
not change from purple to yellow. If  $\text{PtCl}_2(\text{PhCN})_2$  remains in the reaction mixture, it is reduced by added  $\text{SmI}_2$  immediately and the purple color of  $\text{SmI}_2$  disappears and changes to yellow. The reaction mixture was allowed to warm up to room temperature followed by concentration in vacuo to give  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  in 82% yield. In the reported method [1], the  $\text{PtCl}_2(\text{cod})$  was reduced by  $\text{Li}_2(\text{cot})$  in the presence of 2-norbornene to give  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  in 45% yield. Thus, Eq. (1) is the much more efficient and convenient method than the literature method.



Similarly,  $\text{Pt}(\text{cod})_2$  could be also prepared. To obtain  $\text{Pt}(\text{cod})_2$  in better yield, the reduction of  $\text{PtCl}_2(\text{cod})$  was carried out in a mixture of COD and  $\text{CH}_2=\text{CHSiMe}_3$  (Eq. (2)). Although the yield of  $\text{Pt}(\text{cod})_2$  is comparable to that via the reduction by  $\text{Li}_2(\text{cot})$ , our method is much more convenient as mentioned above. In the absence of  $\text{CH}_2=\text{CHSiMe}_3$ , the yield of  $\text{Pt}(\text{cod})_2$  dropped to 23% [7]. The role of  $\text{CH}_2=\text{CHSiMe}_3$  in Eq. (2) is not clear. It is possible that this olefin would temporarily trap a reduced platinum species formed from  $\text{PtCl}_2(\text{cod})$  and  $\text{SmI}_2$  before the second COD molecule gets coordinated to platinum atom, preventing the reduced species from decomposing to metallic platinum. Vinylsilanes are known to form Pt(0) complex, e.g.  $\text{Pt}_2\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_3$  and  $(\text{PR}_3)_3\text{Pt}\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}$  ( $\text{R} = \text{tBu}, \text{Cy}$ ). [8].  $\text{PtCl}_2(\text{PhCN})_2$  was not a good starting complex for the synthesis of  $\text{Pt}(\text{cod})_2$  with  $\text{SmI}_2$ . The red slurry was immediately formed even in the presence of COD and the expected complex was not obtained.

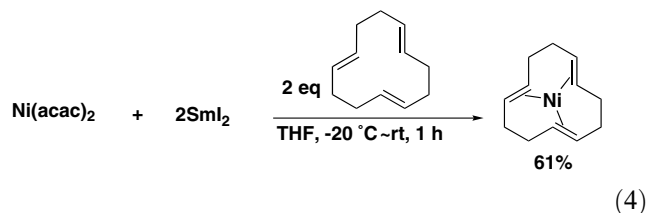


The effect of the addition of  $\text{CH}_2=\text{CHSiMe}_3$  implied that this method would be appropriate for the preparation of  $\text{Pt}_2\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_3$  as well. In fact, the reduction of  $\text{PtCl}_2(\text{cod})$  with  $\text{SmI}_2$  in the presence of  $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$  under a similar condition to Eq. (2) gave  $\text{Pt}_2\{(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_3$  in 69% yield in the following equation:



It is known that hydrosilanes can also be a reducing agent for Pt(II) complexes to give Pt(0) complexes [2]. To compare the utility of our method and reduction by hydrosilanes, the reaction of  $\text{PtCl}_2(\text{PhCN})_2$  with triphenylsilane in the presence of 10 equivalent of norbornene, which was a reported procedure to synthesize tris(styrene)platinum [2a], was performed. Tris(2-norbornene)platinum could not be isolated by this reported method due to its good solubility in common organic solvents, while the formation of tris(norbornene)platinum in 40% yield was confirmed by NMR monitoring. On the other hand, the reaction of  $\text{PtCl}_2(\text{cod})$  with triphenylsilane in the presence of 10 equivalent of COD did not give any product, as was briefly described in the literature [2a].

We tried to apply the  $\text{SmI}_2$  reduction to prepare Ni(0) complexes as well. Under a similar condition to Eq. (1), Ni(cdt) (CDT = *trans, trans, trans*-1,5,9-cyclododecatriene) could be formed in 61% yield (determined by NMR). Ni(cdt) complex has been prepared by use of diethylaluminum ethoxide as a reducing agent with the longer reaction time (10 h) [9]. Therefore, our method is efficient and convenient not only for platinum complexes but for nickel complex.



In summary, we demonstrated the very convenient and simple colorimetric reduction with  $\text{SmI}_2$  for the synthesis of platinum olefin complexes,  $\text{Pt}(\text{C}_7\text{H}_{10})_3$  and  $\text{Pt}(\text{cod})_2$ . This method involves dropwise addition of a solution of  $\text{SmI}_2$  to Pt(II) complex and observation of the color change of the reaction mixture.

### 3. Experimental

**General.** All manipulations were conducted under a nitrogen atmosphere using standard Schlenck or dry box techniques.  $^1\text{H}$  nuclear magnetic resonance spectra were recorded on a JEOL GSX-270S spectrometer. The chemical shifts in the  $^1\text{H}$  magnetic resonance spectra were recorded relative to  $\text{Me}_4\text{Si}$ ,  $\text{C}_6\text{D}_6$  ( $\delta$  7.16) or  $\text{CD}_2\text{Cl}_2$  ( $\delta$  5.32).

**Materials.** All solvents used in this work were distilled prior to use. THF, hexane and  $\text{C}_6\text{D}_6$  were distilled from sodium benzophenone ketyl, acetonitrile and  $\text{CD}_2\text{Cl}_2$  from  $\text{CaH}_2$ . All commercially available materials were distilled and degassed prior to use. A THF solution of  $\text{SmI}_2$  (0.1 M) was prepared by the literature method [10], while a similar reagent supplied by Aldrich Chemical Company, Inc. was also available for our method.

Metallic Sm was purchased from Kojundo Chemical Lab Co. Ltd., as a suspension in spindle oil. An acetonitrile solution of SmI<sub>2</sub> was prepared by dissolving the solids of SmI<sub>2</sub> in acetonitrile, which was prepared by removing volatile materials from a THF solution of SmI<sub>2</sub> in vacuo. PtCl<sub>2</sub>(PhCN)<sub>2</sub> [11] and Pt(cod)Cl<sub>2</sub> [12] were prepared by the literature methods. Celite filtrations were performed by using a plug of Hyflo Super Gel (Wako) over glass wool in disposal pipets or alone on glass filter under vacuum.

### 3.1. Synthesis of tris(2-norbornene)platinum complex [Pt(C<sub>7</sub>H<sub>10</sub>)<sub>3</sub>]

To a suspension of PtCl<sub>2</sub>(PhCN)<sub>2</sub> (983.2 mg, 2.082 mmol) in 10 ml of acetonitrile was added 2-norbornene (5.88 g, 62.46 mmol). The mixture was treated dropwise with an acetonitrile solution of SmI<sub>2</sub> (41.6 ml, 4.164 mmol) at –20 °C. At the beginning of the reaction, the purple color of SmI<sub>2</sub> disappeared immediately after each addition to give yellow suspension. Addition of SmI<sub>2</sub> was continued until no more color change occurred. The mixture was warmed to room temperature and stirred for a further 1.5 h and then the solvent was removed in vacuo until the residue was completely dry. Extraction with hexane gave a brown solution, which was filtered through a column of Celite. A small amount of charcoal was added to the solution and then the charcoal was filtered off. The solvent was removed in vacuo to give off-white solid. Tris(2-norbornene)platinum (815.3 mg, 1.707 mmol) thus prepared was suitable for many purposes (82% yield). The pure material was obtained as colorless needles in 50% yield by dissolving the crude material in hexane and cooling to –30 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.22 (m, 2H), 1.56 (m, 12H), 2.96 (m, 6H), 3.33 (m, *J*<sub>HPt</sub> = 64.0 Hz, 6H).

### 3.2. Synthesis of bis(1,5-cyclooctadiene)platinum complex [Pt(cod)<sub>2</sub>]

A suspension of PtCl<sub>2</sub>(cod) (304.3 mg, 0.813 mmol) in 3 ml of COD (2.6 g, 24.5 mmol) and 3 ml of CH<sub>2</sub>=CHSiMe<sub>3</sub> (2.1 g, 20.5 mmol) was treated dropwise with a THF solution of SmI<sub>2</sub> (17 ml, 1.7 mmol) at –20 °C. At the beginning of the reaction, the purple color of SmI<sub>2</sub> disappeared immediately after each addition to give yellow suspension. Addition of SmI<sub>2</sub> was continued until no more color change occurred. The mixture was warmed to room temperature and stirred for a further 1.5 h and then the solvent was removed in vacuo until the residue was completely dry. Extraction with hexane gave a brown solution, which was filtered through a column of Celite. The solvent was removed in vacuo to give off-white solid. Bis(1,5-cyclooctadiene)platinum (174.7 mg, 0.425 mmol) thus prepared was suitable for many purposes (52% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.19 (m, 16H), 4.2 (m, *J*<sub>HPt</sub> = 55 Hz, 8H).

### 3.3. Synthesis of rac-tris(divinyltetramethyldisiloxane)diplatinum [Pt<sub>2</sub>{(CH<sub>2</sub>=CHSiMe<sub>2</sub>)<sub>2</sub>O}<sub>3</sub>]

To a suspension of PtCl<sub>2</sub>(cod) (30.1 mg, 0.080 mmol) in 2 ml of THF was added 0.3 ml of (CH<sub>2</sub>=CHSiMe<sub>2</sub>)<sub>2</sub>O (243.3 mg, 1.305 mmol). The mixture was treated dropwise with a THF solution of SmI<sub>2</sub> (1.6 ml, 0.16 mmol) at –20 °C. At the beginning of the reaction, the purple color of SmI<sub>2</sub> disappeared immediately after each addition to give yellow suspension. Addition of SmI<sub>2</sub> was continued until no more color change occurred. The reaction mixture was warmed to room temperature and stirred for a further 1 h and then the solvent was removed in vacuo until the residue was completely dry. Extraction with hexane gave a colorless solution, which was filtered through a column of Celite. The solvent was removed in vacuo to give colorless oil (26.3 mg) in 69% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ –0.25, –0.13, 0.15, 0.30, 0.51, 0.52 (each s, 6H, SiMe), 2.84–3.88 (18 overlapping multiplets).

### 3.4. Synthesis of (trans, trans, trans-1,5,9-cyclododecatriene)nickel [Ni(cdt)]

To a solution of Ni(acac)<sub>2</sub> (43.5 mg, 0.169 mmol) and CDT (55.0 mg, 0.339 mmol) in 2 ml of THF was treated dropwise with a THF solution of SmI<sub>2</sub> (3.3 ml, 0.33 mmol) at –20 °C. At the beginning of the reaction, the purple color of SmI<sub>2</sub> disappeared immediately after each addition to give orange suspension. Addition of SmI<sub>2</sub> was continued until no more color change occurred. The mixture was warmed to room temperature and stirred for a further 1 h and then the solvent was removed in vacuo until the residue was completely dry. Extraction with toluene gave orange solution, which was filtered through a column of Celite. The solvent was removed in vacuo to give orange solids. All solids were resolved in C<sub>6</sub>D<sub>6</sub> and NMR measurement was performed. The yield of Ni(cdt) was estimated to be 61%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.66 (s), 4.30 (s).

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