

SYNTHESIS AND CATALYTIC BEHAVIOR OF POLYSILOXANE-SUPPORTED FULLERENE PLATINUM OR RHODIUM COMPLEXES*

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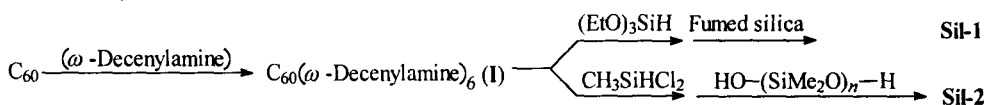
Abstract Two polysiloxanes with pendant fullerene moieties and their platinum or rhodium complexes have been prepared from C_{60} via amination with ω -decenylamine, followed by hydrosilylation with triethoxysilane and immobilization on fumed silica or by hydrosilylation with methylchlorosilane and polycondensation with polydimethylsiloxanol, and then by reacting them with potassium chloroplatinite or rhodium chloride in acetone respectively under argon atmosphere. It was found that the four noble metal complexes are effective catalysts for the hydrosilylation of olefins with triethoxysilane. The regioselectivity of platinum complexes for styrene increases remarkably by introducing C_{60} moiety. Factors influencing catalytic activity and the mechanism have been investigated.

Keywords Functionalized polysiloxane, Fullerene, Hydrosilylation catalyst, Regioselectivity, Hydrosilylation mechanism

INTRODUCTION

Study on the catalytic behavior of fullerenes or their derivatives is one of the stress fields in fullerene science^[1]. It was found that some fullerene metal complexes and compounds exhibited good catalytic activity toward hydrogenation^[2, 3], hydrosilylation^[4-6], and some C_{60} -base catalysts possess special catalytic activity^[3, 6]. However, no paper concerning the catalytic behavior of polymer-bound fullerene metal complexes has appeared up to now.

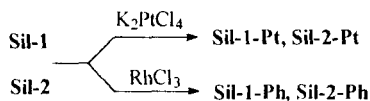
It is well known that polymer-supported metal complexes have the advantages of high activity and selectivity of homogeneous catalysts and ease of separation and recovery of heterogeneous catalysts. The latter is of special interest when C_{60} is used to construct the catalyst because of the expensive cost of fullerene. In this paper, we report the synthesis of four platinum or rhodium complexes of polysiloxane-supported fullerene and their catalytic behavior in the hydrosilylation of olefins. The synthetic routes are depicted below:



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EXPERIMENTAL

IR, NMR, and XPS spectra were obtained on a 170SX FT-IR, a EM-360L spectrometer, and a Kratos XSAM 800 electron energy spectrometer, respectively. Elemental analysis was carried out on a Model 1106 Elemental Auto-Analyzer. GLC was performed on a Model 102G instrument with a thermal conductivity detector, SE-30 stationary phase and silylated white matrix. Fumed silica (specific surface, 150~200 m²/g), fullerene (C₆₀) (purity > 99.5) was obtained from the Jinzhou Chemical Factory and the Institute of Fullerene Research of Wuhan University, respectively. Tri-ethoxysilane and ω -decenylamine were prepared as reported before^[7]. Other chemicals used were A. R. grade reagents.

Synthesis of C₆₀ (ω -Decenylamine)₆

A mixture of C₆₀ (20 mg, 0.028 mmol), ω -decenylamine (200 mg, 1.30 mmol) and 5 mL of benzene was stirred at room temperature under argon for 3 days. No unreacted C₆₀ was found by TLC. The excess ω -decenylamine and benzene were evaporated off. The crude product was dissolved in 1 mL of CHCl₃ and precipitated with methanol (25 mL). After centrifugation, the brown solid was washed with methanol (twice) and dried under vacuum at room temperature for 12 h. The yield was 33.3 mg. Elemental analyses (found, %: C 73.25, H 7.65, N 5.13) indicated that the average number of ω -decenylamine added was 6. IR (KBr/cm⁻¹): 3300, 3071, 2925, 2851, 1696, 1638, 1459, 1413, 1366, 1301, 1240, 1113, 992, 908, 757 and 722. ¹H-NMR (CDCl₃, TMS, δ): 5.5~6.0 (1 H, *m*, =CH—), 4.8~5.3 (2 H, *t*, =CH₂), 2.5~3.4 (1 H, *s*, H-C₆₀), 1.8~2.2 (2 H, *d*, =C—CH₂—), 1.0~1.8 (12 H, *s*, —CH₂—); 0.8~1.0 (1 H, *s*, —NH—, disappeared after adding D₂O).

Synthesis of Silica Polysiloxane-Supported Fullerene (Sil-1)

A mixture of **I** (40 mg, 0.024 mmol), triethoxysilane (0.7 mL, 1.06 mmol), and tetrakis-(triphenylphosphine)platinum complex (2 mg, 1.6×10⁻³ mmol) was stirred at 80°C for 72 h. The cooled mixture was filtered through a sintered glass funnel in which alumina was packed to a height of 2 cm. The alumina was washed with absolute ether. The filtrate was combined with washings, and concentrated. A red-brown viscous oil (58 mg) was obtained. Its ¹H-NMR spectrum showed that no peak of protons on double bond appeared but a peak of $\delta = 0.5$ (*t*, Si-CH₂) appeared. ¹H-NMR (CDCl₃, TMS, δ): 3.30~3.90 (6 H, *m*, OCH₂—), 2.4~3.4 (1 H, *s*, H-C₆₀), 0.9~1.8 (27 H, *s*, —CH₂—, CH₃), 0.8~1.0 (1 H, *s*, —NH—, disappeared after adding D₂O) and 0.4~0.6 (2 H, *m*, Si-CH₂); The obtained product was used directly without further purification.

A mixture of the above viscous oil (58 mg), fumed silica (200 mg) and 10 mL of toluene was stirred at reflux temperature for 12 h and for additional 10h after adding 5 mL of distilled water. The solid product was filtered, dried at 110°C /50 Pa for 5 h, and then transferred to a Soxhelt apparatus and extracted with acetone for 10 h. After drying and grinding, silica-supported polysiloxane with pendent fullerene moiety was obtained as a slightly yellow powder (242 mg). Found (%): C 19.36, H 2.13, N 0.56. The fullerene (C₆₀) content was 47.2 mg/g calculating from the elemental analyses. FT-IR (KBr/cm⁻¹): 3380, 2928, 1635, 1438, 1384, 1103, 963, 805 and 470.

Synthesis of Polysiloxane-Bounded Fullerene (Sil-2)

A mixture of **I** (40 mg, 0.024 mmol), methylchlorosilane (94.3 mg, 0.82 mmol), 5 mL of benzene and two drops of 0.1 mol/L H₂PtCl₆-*i*-PrOH solution was stirred at ambient temperature for 2 h, then at reflux temperature for 6 h. After removing benzene and excess methylchlorosilane, a

slightly brown viscous liquid was obtained (49.2 mg). Its PMR spectra showed that the peak of proton attached to the double bond disappeared and a peak around $\delta = 0.5$ (Si-CH₂) was presented. ¹H-NMR (CDCl₃, TMS, δ): 2.6~3.5 (1 H, s, H-C₆₀), 1.0~1.8 (18 H, s, -CH₂-), 0.8~1.0 (1 H, s, -NH-, disappeared after adding D₂O) 0.3~0.6 (5 H, m, Si-CH₂, Si-CH₃).

The adduct was dissolved in 5 mL of benzene, then added dropwise to a stirred solution composed of silanol-terminated polydimethylsiloxane (75 mg, 0.15 mmol, $M = 500$) and 5 mL of THF under argon atmosphere. After stirring for 10 h, 0.5 mL of trimethylchlorosilane was added, and the stirring was continued for additional 10 h. The solvent and excess trimethylchlorosilane were distilled off under reduced pressure, the solid product was washed with CH₂Cl₂, water, and acetone successively. Then the polysiloxane with fullerene moiety (Sil-2) was obtained as a pale brown powder (118 mg). Found (%): C 16.58, H 1.96, N 0.23. The fullerene (C₆₀) content was 19.4 mg/g. FT-IR (KBr/cm⁻¹): 3360, 2964, 2929, 2851, 1650, 1409, 1262, 1088, 1028, 800 and 461.

Synthesis of Platinum, Rhodium Complexes

A mixture of the polymer ligand Sil-1 (100 mg), potassium chloroplatinite (15.6 mg, 0.36 mmol) and acetone (20 mL) was stirred at reflux temperature under argon for 72 h. After washing with acetone, distilled water and acetone successively, the product was dried at 110°C/50 Pa, Sil-1-Pt was obtained as a pale yellow powder (113.7 mg). Elemental analysis (%): C 18.17, H 2.01, N 0.53, Pt 3.12.

The other metal complexes were prepared similarly. Elemental analysis (%): Sil-1-Rh: C 18.39, H 2.04, N 0.53, Rh 2.53. Sil-2-Rh: C 16.03, H 1.88, N 0.22, Pt 2.03. Sil-2-Rh: C 16.21, H 1.91, N 0.22, Rh 1.36.

RESULTS

The structures of polysiloxane-supported fullerene and their platinum or rhodium complexes were characterized by elementary analysis, FT-IR and XPS. The XPS data are listed in Table 1.

Table 1 XPS data of polymer ligands and platinum, rhodium complexes

Sample	Binding energy (eV)				Sample	Binding energy (eV)			
	Pt _{4f7/2}	Rh _{3d}	N _{1s}	Cl _{2p}		Pt _{4f7/2}	Rh _{3d}	N _{1s}	Cl _{2p}
Pt foil	71.3				Sil-2			399.4	
K ₂ PtCl ₄	73.3			199.4	Sil-1-Pt	72.8		399.8	188.8
Rh		307.0			Sil-2-Pt	72.9		399.8	188.6
RhCl ₃		310.0		199.2	Sil-1-Rh		309.0	399.9	188.7
Sil-1			399.4		Sil-2-Rh		309.1	399.9	188.7

These results indicate that the binding energies of platinum in Sil-1-Pt, Sil-2-Pt are 0.5 eV and 0.4 eV less than that in K₂PtCl₄, and 1.5 eV and 1.6 eV more than that in platinum foil, respectively. And they also indicate that the binding energies of rhodium in Sil-1-Rh, Sil-2-Rh are 1.0 eV and 0.9 eV less than that in RhCl₃, and 2.0 eV and 2.1 eV more than in Rh. These can be interpreted as a result of the formation of platinum or rhodium complexes, and both metals play the role of electron acceptor. After coordination with platinum or rhodium, the unpaired electron pair of nitrogen is transferred to metal atoms, the binding energy of nitrogen increases by about 0.4~0.5 eV. The binding energies of Cl_{2p} in polymer-supported metal complexes decrease 0.5~0.7 eV comparing with K₂PtCl₄ or RhCl₃.

It is found that the platinum or rhodium complexes are effective catalysts for the hydrosilylation of olefins with triethoxysilane. Reaction conditions have remarkable influences on the hydrosilylation. The influences of temperature, the amount of complex used and the nature of olefin on catalytic activity were investigated.

Influence of Reaction Temperature

The addition of triethoxysilane to 1-decene was used to test the catalytic activity at a series of selected temperatures. The results are shown in Table 2.

Table 2 Influence of reaction temperature on hydrosilylation yield

T(°C)	Sil-1-Pt			Sil-1-Rh			Sil-2-Pt			Sil-2-Rh		
	IP ^a (min)	t ^b (min)	Yield (%)	IP ^a (min)	t ^b (min)	Yield (%)	IP ^a (min)	t ^b (min)	Yield (%)	IP ^a (min)	t ^b (min)	Yield (%)
70	5	43	73	5	20	68	25	85	60	30	65	60
80	0	30	80	0	10	72	15	75	63	20	40	60
90	0	20	82	0	5	75	5	40	68	5	10	63
100	0	15	83	0	5	78	0	40	74	0	5	65

a) Induction period, b) yield is not increased with time

Conditions: **Sil-1-Pt**: 1.37×10^{-4} mmol of Pt, **Sil-1-Rh**: 1.43×10^{-4} mmol of Rh, **Sil-2-Pt**: 1.25×10^{-4} mmol of Pt, **Sil-2-Rh**: 1.39×10^{-4} mmol of Rh, 1-Decene 5.0 mmol, Triethoxysilane 5.0 mmol

The data show that the platinum complexes exhibit higher activity than the corresponding rhodium complexes, and **Sil-1-Pt**, **Sil-1-Rh** are more active in comparison with **Sil-2-Pt**, **Sil-2-Rh** respectively. It can also be found that the higher the temperature, the shorter the induction period, and the higher the yield of decyltriethoxysilane.

Influence of the Amount of Metal Complex used

The hydrosilylation of 1-decene with triethoxysilane was carried out to investigate the catalytic behavior using various amounts of metal complexes. When **Sil-1-Pt** was used as catalyst, the yield of decyltriethoxysilane remained unchanged (about 82%) in the range of 2.23×10^{-5} to 3.9×10^{-4} mmol of Pt. But the reaction rate became faster with increasing amounts of catalyst used. In fact, when 2.23×10^{-5} or 3.9×10^{-4} mmol of Pt in **Sil-1-Pt** was used, the hydrosilylation proceeded to completion within 50 min, or 15 min at 100°C, respectively

With increasing amounts of **Sil-2-Pt** used, the yield of hydrosilylation product was increased, and the reaction rate became faster. In the presence of 6.82×10^{-5} , 1.22×10^{-4} and 2.16×10^{-4} mmol of Pt in **Sil-2-Pt**, the yield was 70%, 72% and 74%, and the reaction was completed within 60 min, 40 min, 30 min respectively at 90°C.

The similar phenomenon was observed when rhodium complexes used as hydrosilylation catalysts. When the amount of rhodium complex **Sil-1-Rh** used was 1.55×10^{-4} , 3.03×10^{-4} and 6.06×10^{-4} mmol of Rh, the yield was 69%, 72% and 74% at 100°C, respectively. The yield of decyltriethoxysilane was 66%, 67%, 69% at 90°C in the presence of 1.11×10^{-4} , 1.92×10^{-4} and 3.78×10^{-4} mmol of Rh in **Sil-2-Rh**. No remarkable induction period was observed when rhodium complexes were used.

Influence of the Kind of Olefin on the Yield and Structure of Hydrosilylation Adduct

Triethoxysilane was added to 1-decene, 1-dodecene, allyl phenyl ether, methyl undecenoate and styrene respectively to explore the catalytic activity of the metal complexes. All the four kinds of catalysts exhibited high activity for the hydrosilylation of 1-decene and 1-dodecene, but little activity for methyl undecenoate. The platinum complexes also exhibited good activity for hydrosilylation of allyl phenyl ether and styrene, but the activity of rhodium complexes was poor.

The structure of hydrosilylation product was identified with standard sample. The hydrosilylation of terminal olefins (1-decene, 1-dodecene, allyl phenyl ether) catalyzed by platinum or rhodium complex proceeded according to the anti-Markovnikoff rule to give 1-silylkanes. But hydrosilylation of styrene with triethoxysilane in the presence of **Sil-1-Pt** or **Sil-2-Pt** gave the decyltriethoxysilanes consisting of 1- and 2- isomers in a ratio of about 85/15.

Effect of Mercury and Oxygen

When the hydrosilylation was carried out under air or argon atmosphere, no remarkable difference was found, indicating that oxygen did not act as a *co*-catalyst. The similar phenomenon was observed in the presence or absence of excess mercury in air. This fact confirmed that the active component of hydrosilylation reaction was homogeneous in nature, which is in accord with XPS data.

Effect of Addition Sequence of Reactants

It was found that the reaction proceeded faster when olefin was added before the addition of triethoxysilan using Pt complex as catalyst, though the yield was almost the same. But in rhodium-catalyzed hydrosilylation, the inverse effect on reaction rate by addition sequence was observed. When triethoxysilane was added first, the rate became faster. These facts indicated that the mechanism of hydrosilylation reaction catalyzed by rhodium complexes is not the same as that by platinum complexes (see discussion below).

The Recovery and Reusability of Platinum and Rhodium Complexes

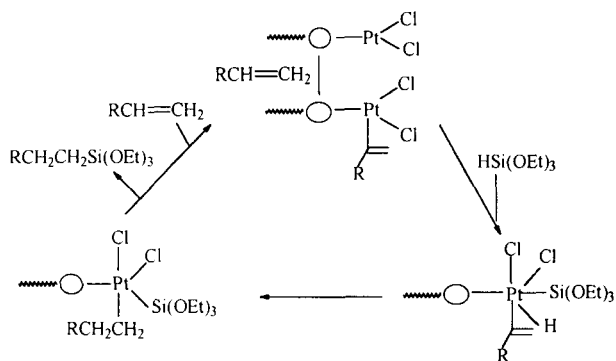
The recovery and reusability properties of the four metal complexes are all excellent. For **Sil-1-Pt** and **Sil-2-Pt**, the yield of decyltriethoxysilane remains unchanged (83%, 80%, respectively) from the first run to the seventh run, and decreased remarkably at the eighth run in both cases. The recovery and reuse ability of rhodium complex are inferior to that of corresponding platinum complexes. When the rhodium complexes were reused, the yield of hydrosilylation product decreased remarkably only after the fourth run.

DISCUSSION

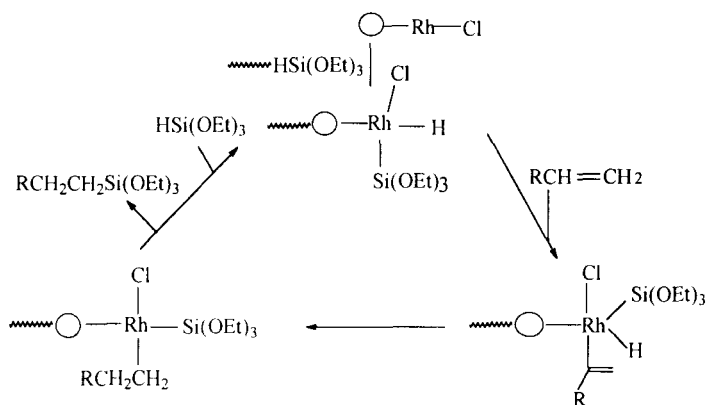
Fullerenes have been of great interest because of their unique spherical structure, conjugate three-dimensional π system, and big volume. It can be expected that C_{60} -base catalysts possess interesting advantages, such as special selectivity. When **Sil-1-Pt** or **Sil-2-Pt** were used as catalysts for the hydrosilylation of styrene with triethoxysilane, the ratio of α - adduct to β - adduct was 85/15 versus 65/35 with a corresponding catalyst without C_{60} moiety. It implied that the regioselectivity is increased remarkably by introducing C_{60} moiety, although the regioselectivity is lower than that of similar monomeric C_{60} -base catalyst (nearly 100%)^[6].

The first question concerning the hydrosilylation mechanism with Pt (or Rh) catalyst is whether the true catalytic species is the polymer-supported platinum (rhodium) complex itself or the monomeric platinum (rhodium) complex leached out from the support. The latter possibility was ruled out by the following experiments: Pt or Rh complex and olefin were stirred at selected temperatures for 30 min, then the catalyst was removed and triethoxysilane was added. No reaction was found to occur within 24 h as shown by GLC, which indicated that the metal remained attached to the polymer ligand throughout the reaction cycle.

There are still two possible pathways for the platinum-catalyzed hydrosilylation. It can proceed through the formation of platinum colloids as the essential step^[8, 9], or according to a Chalk-Harrod mechanism or its modifier^[10, 11]. Chalk and Harrod proposed that the Si-H oxidatively added to an olefin-platinum (II) complex. The hydrosilylation proceeded smoothly with or without Hg in the presence of **Sil-1-Pt** or **Sil-2-Pt** (a diagnostic test to distinguish two mechanisms, when metal colloid is formed, it can selectively amalgamate with Hg, and then loses its whole activity, or at least most of the activity), the characteristic yellow color of platinum colloid was not found in the reaction throughout, dioxygen did not exhibit any *co*-catalytic effect, and there were no observable advantages to adding triethoxysilane first in the sequence of reactants added. These facts all supported the hypothesis that the reaction proceeds according to the Chalk-Harrod mechanism, as described later (Scheme 1).



Scheme 1



Scheme 2

The detailed mechanism of rhodium-catalyzed hydrosilylation was investigated by Marciniak *et al.*^[12]. They pointed out that the reaction involved two distinct stages, the activation of the rhodium precursor by initiating the active intermediates, followed by a very much faster but usual catalytic cycle. In the absence of oxidants, the initial step is the oxidative addition of silane. In our experiments, there was no obvious effect on the activity by adding mercury; no evidence of leachability of metal was observed; and the hydrosilylation proceeded faster by adding triethoxysilane before olefin. All these facts suggest that the catalytic cycle possesses a similar mechanism as described (Scheme 2).

Reference

- 1 Han, W.S., Chemistry Bulletin (in Chinese), 1997, (4): 61
- 2 Nagashima, H., Nakaoka, A., Saito, Y., Kato, M., Kawanish, T. and Itoh, K., J. Chem. Soc., Chem. Commun., 1992, (4): 377
- 3 Liu, Y., Zhao, Z.Y., Liu, S.M. and Yin, Y.Q., J. Mol. Catal (in Chinese), 1996, 10(4): 257
- 4 Chen, Y.Y., Sheng, R.S. and Liu, Y., Chem. Res. Chinese Universities, 1994, 10(4): 338
- 5 Liu, Y., Chen, Y.Y. and Sheng, R.S., Chinese J. Catal. (in Chinese), 1997, 18(2): 91
- 6 Chen, Y.Y., Fang, P.F. and Zhu, L., Chem. J. Chinese Universities, 1998, 19(7): 1011
- 7 Zhang, L.F., Fang, P.F. and Chen, Y.Y., Chem. Reage. (in Chinese), 1997, 19(1): 26
- 8 Harrod, J.F. and Chalk, A.J., J. Am. Chem. Soc., 1964, 86: 1776
- 9 Chalk, A.J. and Harrod, J.F., J. Am. Chem. Soc., 1965, 87: 16
- 10 Lewis, L.N. and Lewis, N., J. Am. Chem. Soc., 1986, 108: 7228
- 11 Lewis, L.N., J. Am. Chem. Soc., 1990, 112: 5998
- 12 Marciniak, J.B., Duczmal, W., Urbaniak W. and Sliwińska, E., J. Organomet. Chem., 1990, 385: 319