



(Dicyclopentadiene) platinum(II) dichloride: An efficient catalyst for the hydrosilylation reaction between alkenes and triethoxysilane

Huarui Wu^a, Chaoyue Zheng^a, Naiwu Chen, Jie Zhu, Deqing Gao^{*}

Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, PR China

ARTICLE INFO

Article history:

Received 8 January 2017

Revised 3 March 2017

Accepted 7 March 2017

Available online 9 March 2017

Keywords:

(Dicyclopentadiene) platinum(II) dichloride

Hydrosilylation catalyst

Aminated alkenes

Triethoxysilane

Functionalized alkenes

ABSTRACT

(Dicyclopentadiene) platinum(II) dichloride was found to be an efficient hydrosilylation catalyst (homogeneous) upon a wide variety of functionalized alkenes and alkenes terminated with chemical moieties (diphenyl amino-, *N*-carbazol- and *N*-isoindoline-1,3-dione-). It is noteworthy that the hydrosilylation of aminated alkenes with triethoxysilane exhibited the yield of over 70% and the selectivity (γ -isomer/ β -isomer) of more than 3/1. Due to steric hindrance lowering Markovnikov probability, the alkenes with big terminal moieties (diphenyl amino-, *N*-carbazol- and *N*-isoindoline-1,3-dione-) presented the high ratio of anti-Markovnikov isomers. The strategy of the hydrosilylation of the protected diamino chelating alkene was developed.

© 2017 Elsevier Ltd. All rights reserved.

Introduction

The hydrosilylation reaction is a very important synthetic method for the preparation of organo-silicon compounds in the silicone industry.^{1–3} Transition metal catalysts are commonly used in the hydrosilylation reaction.^{4,5} Among various transition metal catalysts, platinum catalysts, for example, hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Speier's catalyst),⁶ and Karstedt's catalyst,⁷ are very effective in the hydrosilylation reaction.^{8,9}

The yield and the selectivity of the catalyzed hydrosilylation processes depend not only on the performance of the catalyst but also on the nature of the alkene itself. It was observed that the platinum-catalyzed hydrosilylation of primary allyl amines had the formation of hydrogen and presumably aminosilanes,¹⁰ and the type of the reactions could be carried out at high reaction temperatures and pressure, or in the presence of reaction promoters.¹¹ Quite recently, Charles Mioskowski et al. tested the hydrosilylation of different aminated alkenes substrates with methyldiethoxysilane reagent and found that PtO_2 was superior to other platinum catalysts (Speier's catalyst and Karstedt's catalyst) in terms of the yield and selectivity.¹²

Triethoxysilane is an important hydrosilylation reagent of olefins for the synthesis of various organosilicon compounds.^{13–17}

There are a few of reports on alkene hydrosilylation with triethoxysilane in the presence of nickel catalysts,¹⁸ rhodium catalyst,¹⁹ ruthenium catalyst,²⁰ platinum catalysts.^{21,22} However, there is no report on the hydrosilylation catalyst of different aminated alkenes with triethoxysilane reagent.

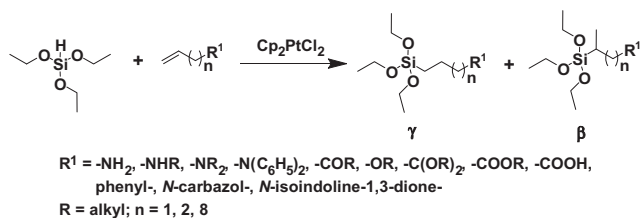
(Dicyclopentadiene) platinum(II) dichloride was reported by several group.^{23–26} The material as a catalyst was applied to the hydrosilylation reaction in which 4-(allyloxy)benzoyl esters were contacted with poly(methylsiloxane),²³ but the systematic study of the catalytic property has not been done. In this paper, we describe the hydrosilylation reaction of different aminated alkenes with triethoxysilane in the presence of the catalyst of (dicyclopentadiene) platinum(II) dichloride, and further extend the hydrosilylation reaction with a series of other functionalized alkenes substrates.

The synthesis of hydrosilylation reaction was carried out by following the general route (Scheme 1): Equimolar amounts of triethoxysilane and a respective functionalized alkene were stirred with 330 ppm (dicyclopentadiene) platinum(II) dichloride (The catalyst was synthesized by following the literature 27) (i.e., 330 μmol per mol of silane) without solvent at 85 °C in a sealed schlenk tube under argon. After cooled to room temperature, the crude was purified by vacuum distillation or silica gel column chromatography to afford the desired product. The yield and the selectivity (i.e., the ratio of γ -isomer/ β -isomer) were calculated on the basis of ^1H NMR spectrum.²⁸

^{*} Corresponding author.

E-mail address: iamdqgao@njtech.edu.cn (D. Gao).

^a The first two authors contributed equally to this work.



Scheme 1. Hydrosilylation reaction of different functionalized alkenes with triethoxysilane.

Results and discussion

The hydrosilylation is a catalytic addition reaction and the ratio of the Markovnikov isomer to the anti-Markovnikov isomer could be determined from 1H NMR spectrum.^{12,29} In the work, the 1H chemical shift of $O-CH_2$ at 3.70–3.75 ppm (q, 6H) was chosen as the characteristic peak of β -isomer,³⁰ and the 1H chemical shift of CH_2-Si at 0.45–0.65 ppm (m, 2H) was chosen as the characteristic peak of γ -isomer.^{12,31} 2,4,6-Trichloronitrobenzene was used as the internal standard from 1H NMR spectrum. The determinations of the yield and the ratio of γ - to β -isomers were based on the following equation:²⁸

$$P(x) = P(std) \cdot \frac{MW(x)}{MW(std)} \cdot \frac{nH(std)}{nH(x)} \cdot \frac{m(std)}{m(x)} \cdot \frac{A(x)}{A(std)}$$

where $m(x)$ and $m(std)$ are the masses (weights) in g, $MW(x)$ and $MW(std)$ are the molecular weights in g/mol, $P(x)$ and $P(std)$ are the purities, $nH(x)$ and $nH(std)$ are the number of protons generating the selected signals for integration, $A(x)$ and $A(std)$ are the areas for the selected peaks of the analyte and the internal standard, respectively. The integration area was obtained from the respective characteristic peak in 1H NMR spectrum and the purity $P(x)$ which stands for the yield was calculated for each isomer and the ratio of γ - to β -isomers was correspondingly determined. The results of the hydrosilylation of different aminated alkenes are shown in Table 1.

As shown in Table 1, all six aminated alkenes reacted with triethoxysilane in the presence of the catalyst of (dicyclopentadiene) platinum(II) dichloride and the yield was higher than 70%. The γ -isomer is often the desired product in the hydrosilylation of allyl derivatives.³² As indicated in Table 1, the hydrosilylation with (dicyclopentadiene) platinum(II) dichloride catalyst showed the high selectivity and the ratio of γ -isomer/ β -isomer was more than 3/1.

Table 1
(Dicyclopentadiene) platinum(II) dichloride catalyst for the hydrosilylation of different aminated alkenes with the triethoxysilane reagent.

Entry	Alkene	Reaction time(h)	Yield ^a (%)	Ratio ^a (γ/β)
1		20	84	92/8
2		20	73	84/16
3		20	74	94/6
4		20	91	83/17
5		20	76	78/22
6		20	81	98/2

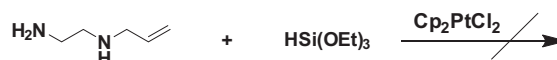
^a Calculated on the basis of 1H NMR spectrum.

Table 2

Different Pt-catalysts for the hydrosilylation of compound 1 with the triethoxysilane reagent.

Entry	Catalyst	reaction time(h)	Yield ^a (%)	Ratio ^a (γ/β)
1	(Dicyclopentadiene) platinum(II) dichloride	20	81	88/12
2	Karstedt catalyst	20	83	89/11
3	$H_2PtCl_6 \cdot 6H_2O$	20	34	73/22
4	PtO_2	20	0	/

^a Calculated on the basis of 1H NMR spectrum.

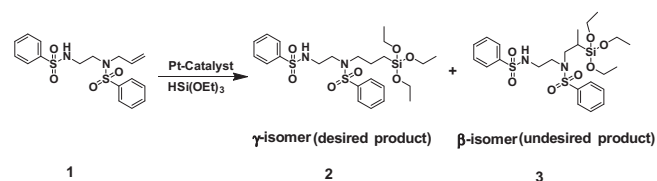


Scheme 2. (Dicyclopentadiene) platinum(II) dichloride catalyst for the hydrosilylation of the diamino chelating alkene with triethoxysilane.

For the primary allylamine (entry 1), (dicyclopentadiene) platinum(II) dichloride catalyzed the hydrosilylation reaction with the yield of 84% and the selectivity (γ -isomer/ β -isomer) of 92/8. For the secondary allylamines, when the length of the alkyl chain was increased with three-carbon chain longer (entry 2 vs. entry 5), the catalysis reaction exhibited a small change in terms of the yield and the selectivity. The yield and the selectivity were changed from 73% and 84/16 (entry 2) to 76% and 78/22 (entry 5), respectively. The hydrosilylation reaction of *N*-ethyl-2-methylallylamine (entry 4) showed the highest yield of 91%. For the tertiary allylamine (entry 3), the hydrosilylation reaction of *N,N*-dimethylallylamine with triethoxysilane presented the high selectivity of 94/6 and a modest yield of 74%. In contrast, the tertiary aromatic amine (entry 6) exhibited even higher selectivity with the γ -isomer/ β -isomer ratio of 98/2, perhaps due to the steric hindrance of two big phenyl groups lowering Markovnikov probability. Compared with PtO_2 ,¹² the homogeneous (dicyclopentadiene) platinum (II) dichloride catalyst in the work showed the higher selectivity (γ -isomer/ β -isomer), i.e., 84/16 of entry 2 and 78/22 of entry 5 in Table 1 in the work versus 44/56 of entry 2 and 50/50 of entry 5 in Table 2.¹² It is confirmed that (dicyclopentadiene) platinum(II) dichloride can efficiently catalyze the hydrosilylation reaction of the monoamino alkenes.

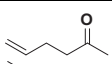
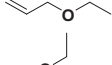
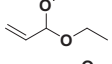
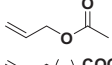
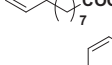
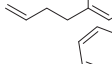
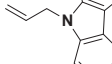
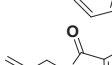
Amino function is easy to result in catalyst poisoning by forming a complex with catalyst metal ion,¹² or by acid base interaction in the case of the strongly acidic Speier's catalyst.³³ As reported in the literature 12, PtO_2 or $H_2PtCl_6 \cdot 6H_2O$ could not catalyze the hydrosilylation of a strong ligand diamino chelating alkene. We tested the substrate with (dicyclopentadiene) platinum(II) dichloride by following the above-developed hydrosilylation procedure, but the reaction failed (Scheme 2).

What occurred to us was to first protect the amino groups. The benzylsulfonyl was chosen as the protected group and the synthesis of protected compound 1 was described in Supporting Information in detail. Three catalysts, Karstedt's catalyst, $H_2PtCl_6 \cdot 6H_2O$,



Scheme 3. Pt-catalyst for the hydrosilylation of the diamino chelating alkene which is protected by the benzylsulfonyl group with triethoxysilane.

Table 3
Hydrosilylation reaction with triethoxysilane on various functionalized alkenes.

Entry	Alkene	Reaction time(h)	Yield ^a (%)	Ratio ^a (γ/β)
1		20	95	95/5
2		20	76	87/13
3		20	99	77/23
4		20	95	97/3
5		20	93	88/12
6		20	79	77/23
7		20	82	98/2
8		20	93	96/4

^a Calculated on the basis of ¹H NMR spectrum.

PtO₂ and (dicyclopentadiene) platinum(II) dichloride, were used for the hydrosilylation of compound **1** with triethoxysilane reagent (Scheme 3).

As indicated in Table 2, the catalysis efficiency of the hydrosilylation reaction between (dicyclopentadiene) platinum(II) dichloride and Karstedt's catalyst was comparable. The yield and the selectivity were 81% and 88/12 with (dicyclopentadiene) platinum(II) dichloride catalyst, and 83% and 89/11 with Karstedt's catalyst, respectively. H₂PtCl₆·6H₂O catalyst was relatively weak. The yield and the selectivity were only 34% and 73/22, respectively. PtO₂ even did not catalyze the reaction.

Moreover, to further extend the scope of (dicyclopentadiene) platinum(II) dichloride, we also tried to test a series of other functionalized alkenes (–COR, –OR, –C(OR)₂, –COOR, –COOH...) and alkenes terminated with chemical moieties (phenyl-, *N*-carbazol- and *N*-isindoline-1,3-dione-). The experimental data were compiled in Table 3. It is clear that the hydrosilylation reaction could be completed with a high yield (>75%) and a good selectivity (γ-isomer/β-isomer) (>77/23), whatever function (ketone, ether, ketal, ester, or acid) is present on the alkene. In agreement with the result of entry 6 in Table 1, the selectivity of the reaction with large terminal moieties (*N*-carbazol- from entry 7 and *N*-isindoline-1,3-dione- from entry 8) was high.

Conclusions

In summary, the hydrosilylation reaction of a wide variety of functionalized alkenes with triethoxysilane in the presence of

(dicyclopentadiene) platinum(II) dichloride catalyst had been studied. The hydrosilylation reaction of aminated alkenes got high yield and good selectivity. Although it was impossible to directly carry out the hydrosilylation of a diamino chelating alkene with triethoxysilane, after the protection of the amino groups, the hydrosilylation worked well.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under grant No. 21371096.

A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2017.03.017>.

References

- Sanchez JC, Macromol WC. *Chem Phys*. 2008;209:1527–1540.
- Lewis LN, Stein J, Gao Y, Colborn RE, Hutchins G. *Platinum Met Rev*. 1997;41:66–75.
- Troegel D, Stohrer J. *Coord Chem Rev*. 2011;255:1440–1459.
- Aubin S, Le Floch F. *ACS Symp Ser*. 2002;818:334–346.
- Hoffmann F, Wagler J, Böhme U, Roewer G. *J Organomet Chem*. 2012;705:59–69.
- Speier JL, Webster JA, Barnes GH. *J Am Chem Soc*. 1957;79:974–979.
- Karstedt BD, U.S. Patent 3775452 A, 1973.
- Quirk RP, Kim H, Polce MJ, Wesdemiotis C. *Macromolecules*. 2005;38:7895–7906.
- Pagliaro M, Ciriminna R, Pandarus V, Béland F. *Eur J Org Chem*. 2013;6227–6235.
- Saam C, Speier L. *J Org Chem*. 1959;24:119–120.
- Chu NS, Kanner B, Schilling CL, EP135813 B1, 1988.
- Sabourault N, Mignani G, Wagner A, Mioskowski C. *Org Lett*. 2002;4:2117–2119.
- Ma C, Li JY, Peng JJ, et al. *J Organomet Chem*. 2013;727:28–36.
- Sinha AK, Bihari B, Mandal BK, Chen L. *Macromolecules*. 1995;28:5681–5683.
- Bai Y, Peng JJ, Li JY, Lai GQ. *Appl Organomet Chem*. 2011;25:400–405.
- Fetouaki R, Seifert A, Bogza M, Oeser T, Blumel J. *Inorg Chim Acta*. 2006;359:4865–4873.
- Feinle A, Flaig S, Puchberger M, Schubert U, Husing N. *Chem Commun*. 2015;51:2339–2341.
- Pappas I, Treacy S, Chirik PJ. *ACS Catal*. 2016;6:4105–4109.
- Xu Y, Bai Y, Peng JJ, Li JY, Xiao WJ, Lai GQ. *J Organomet Chem*. 2014;765:59–63.
- Liu L, Li XN, Dong H, Wu C. *J Organomet Chem*. 2013;745–746:454–459.
- Li J, Yang CH, Zhang L, Ma TL. *J Organomet Chem*. 2011;696:1845–1849.
- Hu RH, Zha LF, Cai MZ. *Catal Commun*. 2010;11:563–566.
- Apfel MA, Finkelmann H, Janini GM, et al. *Anal Chem*. 1985;57:651–658.
- Stille JK, Fox DB. *J Am Chem Soc*. 1970;92:1274–1278.
- Kharasch MS, Ashford TA. *J Am Chem Soc*. 1936;58:1733–1738.
- Drew D, Doyle JR. In: Cotton FA, editor. *Inorganic Synthesis*, vol. XIII. New York: McGraw-Hill; 1971:47–50.
- Wang YY, Cai J, Rauscher H, Behm RJ, Goedel WA. *Chem Eur J*. 2005;11:3968–3978.
- Rundlof T, Mathiasson M, Bekiroglu S, Hakkarainen B, Bowden T, Arvidsson T. *J Pharmaceut Biomed*. 2010;52:645–651.
- Risangud N, Li ZJ, Anastasaki A, Wilson P, Kempe K, Haddleton DM. *RSC Adv*. 2015;5:5879–5885.
- Kang S, Ono RJ, Bielawski CW. *J Am Chem Soc*. 2013;135:4984–4987.
- Mori H, Miyamura Y, Endo T. *Langmuir*. 2007;23:9014–9023.
- Igarashi M, Matsumoto T, Kobayashi T, et al. *J Organomet Chem*. 2014;749:421–427.
- Jonas G, Stadler R. *Acta Polym*. 1994;45:14–20.