Vietnam Journal of Science and Technology ***62*** *(3) (2024)*

doi:10.15625/2525-2518/18442

Cyclometalated platinum(II) complexes bearing eugenol as effective catalysts for hydrosilylation of phenylacetylene by triethoxysilane

Pham Van Thong[1], Dinh Ngoc Doan Trang[1], Truong Thuy Hang[2], Nguyen Thi Thanh Chi[1,*]

[1]*Department of Chemistry, Hanoi National University of Education, 136 Xuan Thuy, Ha Noi, Viet Nam*

[2]*Hanoi Thang Long Primary and Secondary School, Ha Dong, Ha Noi, Viet Nam*

[*]Emails: *chintt@hnue.edu.vn*

Received: 21 June 2023; Accepted for publication: 16 January 2024

Abstract. The catalytic activities of the platinacyclic complexes bearing eugenol (EugH) including [Pt(μ-Cl)(Eug)]$_2$ (**1**) and [PtCl(Eug)(amine)] (**2**–**4**) [amine: pyridine/**2**, 4-methylpyridine/**3**, quinoline/**4**] for hydrosilylation of phenylacetylene by triethoxysilane have been studied for the first time. The results showed that the complexes **1**–**4** exhibited good catalytic abilities. With loading 0.5 mol% each of the catalysts **1**–**4** at 70 ^{o}C without solvents and any other additives in the air for 2 hours, the triethoxysilane was completely converted to (*E*)-triethoxy(styryl)silane) (β(*E*) – the major product) and (triethoxy(1-phenylvinyl)silane) (α – the minor product) with the α/β(*E*) molar ratio ranging from 1 : 2.6 to 1 : 2.8. At the same reaction conditions with loading 0.1 mol% each of the catalysts **2**–**4,** the conversion of triethoxysilane slightly reduced with an efficiency of 97–99% and the α/β(*E*) molar ratio of 1 : 2.6 indicating the important role of the Pt-(C=C$_{alkene}$) in **1**–**4** for their catalytic activity. Furthermore, the verification of structures of complexes **2**–**4** by ^{13}C NMR spectroscopy indicated that in chloroform-d_1, complex **3** formed two distinct structural forms due to strong intermolecular interactions between the chloroform solvent and the complex, including a Cl$_3$C-H...ClPt(II) hydrogen bond and a Cl$_2$HC-Cl...Pt(II) halogen bond.

Keywords: Platinum complexes, eugenol, hydrosilylation, hydrogen and halogen bonds, NMR.

Classification numbers: 2.6.1, 2.10.2, 2.10.3.

1. INTRODUCTION

Platinum and its complexes are well known for their applications in not only cancer chemotherapy [1, 2] but also in the field of organic synthesis on industrial scales [3, 4]. Prominent among them is the use of platinum complexes containing olefins, including Speier's, Karstedt's and Markó's catalysts (Fig. 1), for the hydrosilylation reactions, which are simple and

atom economical methods to synthesize organosilicon compounds with numerous uses in polymer chemistry and materials science [3]. Nevertheless, these commercial catalysts have either the restricted stability against oxygen and moisture or challenging synthetic procedures [3, 4]. Therefore, new catalysts based on platinum complexes are still being developed by many scientists [5-11].

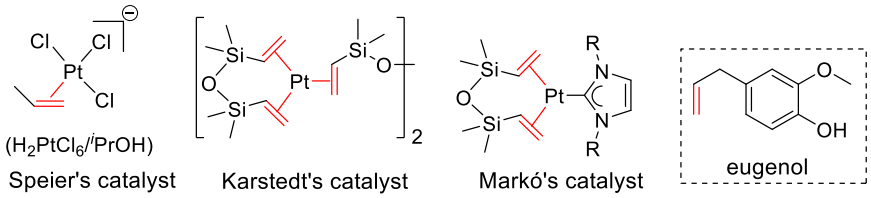


Figure 1. Structures of Speier's, Karstedt's and Markó's catalysts and eugenol.

Eugenol (EugH – Fig. 1) is known as the main component in the essential oils of clove (*Syzygium aromaticum*) and tulsi (*Ocimum sanctum* L.). Recently, eugenol has been introduced into the coordination sphere of diplatinum and monoplatinum complexes [12, 13], which possess a Pt–olefin bond similar to the industrial relevant platinum-based catalytic systems mentioned above. Many of them exhibit high anticancer activities against several human cancer cell lines with IC_{50} values of 8.7-10.8 μM [12]. However, their catalytic activities have not been investigated.

In this paper, we present the results of investigating the catalytic ability of some cyclometalated platinum(II) complexes containing eugenol for the hydrosilylation of phenylacetylene by triethoxysilane.

2. MATERIALS AND METHODS

2.1. Materials

Unless otherwise noted, all operations were performed without taking any precautions to exclude air and moisture. All chemicals were used as received without any further treatment. Phenylacetylene, and triethoxysilane were purchased from Sigma-Aldrich. The complex [Pt(μ-Cl)(Eug)]$_2$ (**1**) was prepared as previously reported [12]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 MHz at 298-300 K, and the chemical shifts (δ) were internally referenced using the residual protio-solvent signals relative to tetramethylsilane.

2.2. Methods

Complexes **2–4** were prepared as previously reported [12] with a minor modification (for details see the SI).

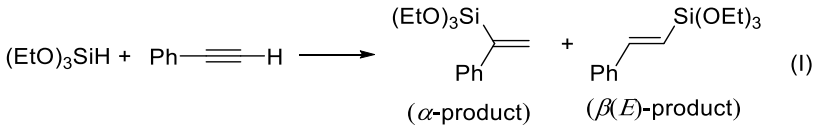
[PtCl(Eug)(pyridine)] (2). Yield: 415 mg (88%). ^{13}C NMR (125.8 MHz, acetone-d_6): 151.5, 148.7, 143.0, 140.9, 139.6, 127.1, 125.0, 121.9, 109.1 (Ar−C), 89.5 (*C*H=CH$_2$), 62.0 (CH=*C*H$_2$), 56.4 (OCH$_3$), 39.2 (CH$_2$).

[PtCl(Eug)(4-methylpyridine)] (3). Yield: 447 mg (92%). ^{13}C NMR (125.8 MHz, acetone-d_6): 151.7, 150.7, 146.4, 143.0, 140.1, 127.7, 125.2, 121.9, 109.0 (Ar−C), 89.2 (*C*H=CH$_2$), 61.8 (CH=*C*H$_2$), 56.4 (OCH$_3$), 39.2 (CH$_2$), 21.0 (CH$_3$).

^{13}C NMR (125.8 MHz, chloroform-d_1): 151.8, 151.2, 150.4, 149.7, 145.1, 144.6, 142.1, 141.7, 140.0, 139.9, 126.9, 126.4, 123.6, 120.2, 117.6, 107.9, 107.5 (Ar−C), 96.0/88.6 (*C*H=CH$_2$), 67.2/61.5 (CH=*C*H$_2$), 56.1/56.0 (OCH$_3$), 39.0/38.8(CH$_2$), 21.4/21.2 (CH$_3$).

*[PtCl(Eug)(quinoline)] (**4**)*. Yield: 470 mg (90%). ^{13}C NMR (125.8 MHz, acetone-d_6): 153.5, 151.2, 146.5, 143.1, 140.0, 131.9, 129.6, 128.7, 128.5, 121.7, 109.2 (Ar−C), 93.9 (*C*H=CH$_2$), 64.0 (CH=*C*H$_2$), 56.5 (OCH$_3$), 39.3 (CH$_2$).

Catalyst **4** (0.5 mol%) was added to a Schlenk tube, followed by triethoxysilane (1.0 mmol, 1.0 equiv) and phenylacetylene (1.2 mmol, 1.2 equiv) in an atmosphere of either argon or air. The Schlenk tube was submerged in an oil bath that had been preheated to the studied temperatures (Table 2). After each set up reaction time, the Schleck tube was removed from the oil bath, the reaction mixture was cooled to room temperature, and the yields as well molar ratios of the product were analyzed by ^{1}H NMR spectroscopy. The same steps were taken when replacing catalyst **4** by each of the catalysts **1**–**3** with 0.5/0.1 mol% loading, but the reaction conditions including temperature, time and atmosphere were fixed at 70°C, 2 hours and under air (Table 2).

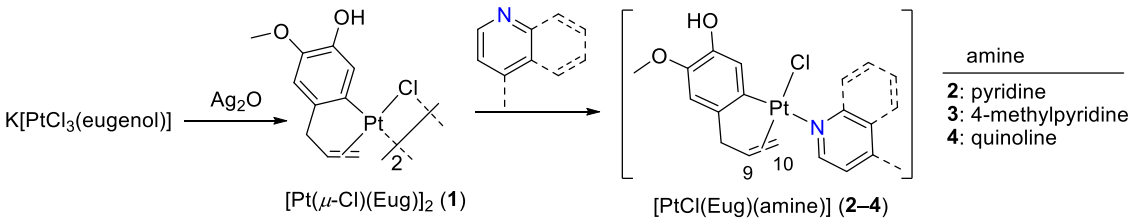


Scheme 1. Hydrosilylation of phenylacetylene by triethoxysilane.

The determination of regiochemistry and stereochemistry of the alkenylsilane isomers in Scheme 1 were based on the olefinic coupling constants in the ^{1}H NMR spectra (for details see the SI) and reference [8-10, 14]. The two doublets at 6.18 and 7.12 ppm with ^3J(H,H) = 19.5 Hz in all the spectra belong to two protons CH=CH of the *β(E)* isomer. Moreover, the two germinal protons =CH$_2$ of the *α*-isomer give rise to two doublets at 5.96 and 6.14 ppm with the ^2J(H,H) = 3 Hz. To perform quantification of each isomer, the olefinic peaks of the products and the H-(Si) peak of the triethoxysilane resonating at 4.25 ppm were integrated.

3. RESULTS AND DISCUSSION

Complexes **1**–**4** were synthesized basing on the method described in [12, 13] with chemical equations as shown in Scheme 2. Their structures have been studied by spectroscopic methods such as ESI-MS, IR, ^{1}H NMR and especially single crystal X-ray diffraction for **2** and **3** [12, 13]. Herein, we recorded ^{13}C NMR spectra of complexes **2**–**4** to confirm their structures. They were recorded in acetone-d_6, for complex **3** was extra recorded in chloroform-d_1. The ^{13}C signals are assigned based on their chemical shifts (δ), intensity and the HSQC spectrum for complex **3** (for details see the SI). The assigned results are presented in the experimental section. The olefinic ^{13}C signals of free eugenol and complexes **2**–**4** are listed in Table 1. Figure 1 shows the partial ^{13}C spectrum of **3** in acetone-d_6 (a) and chloroform-d_1 (b) as an example.



Scheme 2. Preparation of complexes **1**–**4** (the numeration of structures used for NMR analysis).

Figure 2 shows that complex **3** gives only one set of ^{13}C signals in acetone-d_6. However, it presents two sets of signals in chloroform-d_1. Specifically, Fig. 2a shows four signals for C8, OCH_3, C9 and C10 at 39.2, 56.4, 89.2 and 61.8 ppm, respectively. However, in chloroform-d_1 each of these carbons gives rise to two peaks with significantly different chemical shifts, especially for C9 and C10. The presence of two signal sets was also observed in the ^{1}H NMR spectrum of complex **3** measured in chloroform-d_1 in our previous study [12, 13]. This can be explained by the formation of hydrogen and halogen bonds between the chloroform and complex **3** resulting in the existence of two structures **3a** and **3b** as shown in Fig. 2b. This also accords with earlier observations of other authors [12, 13]. Since the solvent acetone does not have these interactions, complex **3** in this solvent exists in a unique structure as indicated in Fig. 2a.

Table 1. Selected ^{13}C signals of free eugenol and complexes **2**–**4**, δ (ppm).

Compound	**C9**	**C10**
EugH[a] [15]	137	110
[PtCl(Eug)(pyridine)] (**2**)[b]	89.5	62.0
[PtCl(Eug)(4-methylpyridine)] (**3**)[b]	89.2	61.8
[PtCl(Eug)(4-methylpyridine)] (**3**)[a]	96.0/88.6	67.5/61.2
[PtCl(Eug)(quinoline)] (**4**) [b]	93.9	64.0

a: chloroform-d_1; b: acetone-d_6.

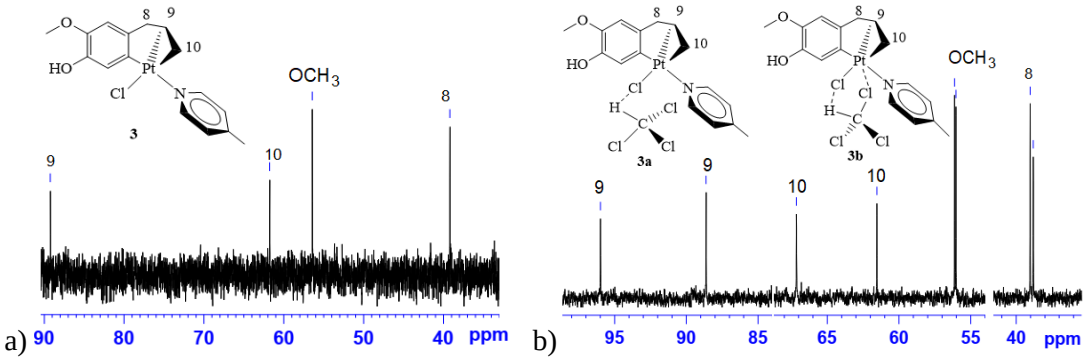


Figure 2. Partial ^{13}C NMR spectrum of complex **3** in acetone-d_6 (a) and chloroform-d_1 (b).

Table 1 shows that the δ values of C9 and C10 in the complexes are both strongly decreased in comparison with those in the free ligand. This elucidates that the eugenol has coordinated with Pt(II) through the C9 and C10 atoms in a η^2 manner [12]. Moreover, the chemical shifts of C9 and C10 in **2** and **3** which were measured in the same solvent, acetone-d_6, are very close to

each other and much smaller than those in **4**. This indicates that the pyridine and 4-methylpyridine weaken the Pt–olefin bond in **2** and **3** much more than the quinoline ligand in **4**.

In further work, we investigated the catalytic ability of monoplatinum complexes **2**–**4** as well as diplatinum complex **1** for the hydrosilylation of phenylacetylene by triethoxysilane. To find out the most effective catalytic conditions, the first step in this work was focused on the optimization of conditions including atmosphere, temperature and time using complex **4** as the catalyst. The results of this optimization are presented in Table 2 (entries 1–5).

In entry 1, the reaction was implemented at 80 °C in argon atmosphere without solvent and any other additives with 0.5 mol% loading of catalyst **4** during 3 h. The absence of the signal at 4.25 ppm for the Si-H of triethoxysilane in the ^{1}H NMR of the product (Fig. 3) demonstrates that the triethoxysilane has been completely transformed. The hydrosilylation products are only *anti*-Markovnikov $\beta(E)$ ((*E*)-triethoxy(styryl)silane) as a major product and Markovnikov α (triethoxy(1-phenylvinyl)silane) as a minor product with the $\alpha/\beta(E)$ molar ratio of 1:2.6 (Table 2 and Fig. 3). The formation of *syn*-Markovnikov $\beta(Z)$ ((*Z*)-triethoxy(styryl)silane) with two olefinic protons resonating at 5.0–7.5 ppm with the ^3J(H,H) value of 14–16 Hz [14] was not observed. To study the effect of atmosphere, in test 2, we fixed all the conditions as in entry 1, only replacing the Ar by the air. Surprisingly, the catalytic efficiency was unchanged. Therefore, in the next tests (entry 3–5), we conducted all the reactions under air with adjusting temperature, time and mol% of the catalyst. The results showed that the highest catalytic activity in the air with the $\beta(E)$ as a major product was found at 70 ^{o}C during 2 h with 0.5 mol% loading of complex **4** (entry 3, table 2).

Table 2. Performances of complexes **1**−**4** in the catalytic reactions (I)[a].

entry	loading of complex (%)	complex	atmosphere	time (h)	T (^{o}C)	conversion[b] (%)	α/β(*E*) ratio	TON[c]	TOF (h^{-1})
1	0.5	**4**	Ar	3	80	100	1:2.6	2.0×10^2	0.7×10^2
2	0.5	**4**	air	3	80	100	1:2.6	2.0×10^2	0.7×10^2
3	**0.5**	**4**	**air**	**2**	**70**	**100**	**1:2.6**	$\mathbf{2.0 \times 10^2}$	$\mathbf{1.0 \times 10^2}$
4	0.1	**4**	air	2	70	99	1:2.6	9.9×10^2	4.95×10^2
5	0.1	**4**	air	1	50	95	1:2.5	9.5×10^2	9.5×10^2
6	0.5	**1**	air	2	70	100	1:2.7	2.0×10^2	1.0×10^2
7	0.5	**2**	air	2	70	100	1:2.7	2.0×10^2	1.0×10^2
8	0.5	**3**	air	2	70	100	1:2.8	2.0×10^2	1.0×10^2
9	0.1	**2**	air	2	70	97	1:2.6	9.7×10^2	4.85×10^2
10	0.1	**3**	air	2	70	97	1:2.6	9.7×10^2	4.85×10^2

[a]Reaction conditions: 1 mmol of triethoxysilane, 1.2 mmol of phenylacetylene. [b]Yields were determined by ^{1}H NMR spectroscopy. [c]Under selected conditions.

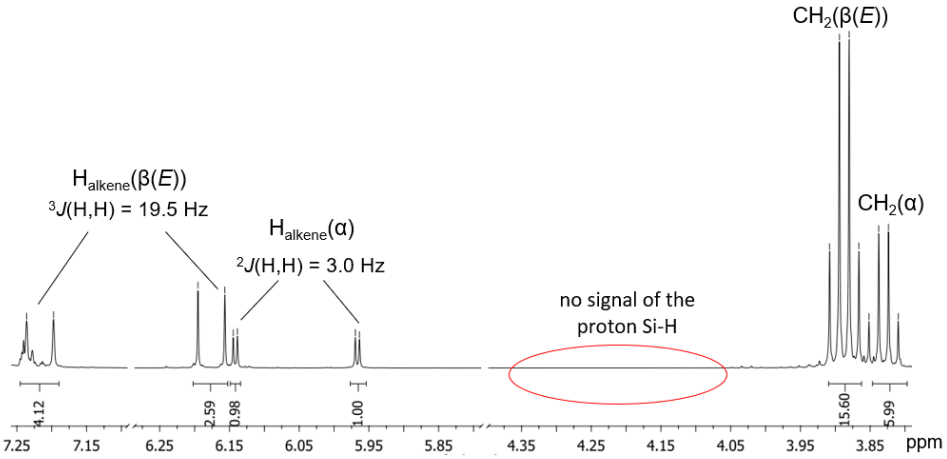


Figure 3. Partial ^{1}H NMR spectrum of the product of entry 1 (Table 2) in chloroform-d_1.

Following the optimization, a variety of different catalysts were tested for 2 hours under air in a Schlenk tube at 70 ^{o}C (entry 6–10). Complexes **1**–**3**, like complex **4**, demonstrated good catalytic activities for the hydrosilylation reaction of phenylacetylene with triethoxysilane under mild conditions with only α and β(*E*) products, the yields up to 100% in entries 6–8. In all tests, the molar ratio α/β(*E*) did not significantly differ within the range of 1/2.7–1/2.8. This indicates that the difference in the amine ligands in complexes [PtCl(Eug)(amine)] has no discernible impact on the catalytic efficiency of the complexes in the tested conditions. Interestingly, the catalytic activity of the diplatinum complex **1** was similar to the monoplatinum complexes **2**–**4** (table 2). This finding can be deduced that the Pt–olefin bond in **1**–**4** has a significant effect on catalytic ability of the complexes.

The smaller amounts of catalysts **2-4** were examined to compare their catalytic activities (entries 4, 9, 10). The results showed that the yields all declined compared to the case of loading 0.5 mol % corresponding catalysts but the change is insignificant (table 2, Fig. 4). In particular, complex **4** is the most active (entry 4, yield of 99%), closely followed by complexes **2** and **3** (entries 9 and 10, yields of 97%). This result shows that the heterocyclic amines in complexes **2**–**4** have no significant effect on their catalytic activities. This corroborates the finding of the important role of eugenol for catalytic activity of the cyclometalated platinum(II) complexes **1**–**4**.

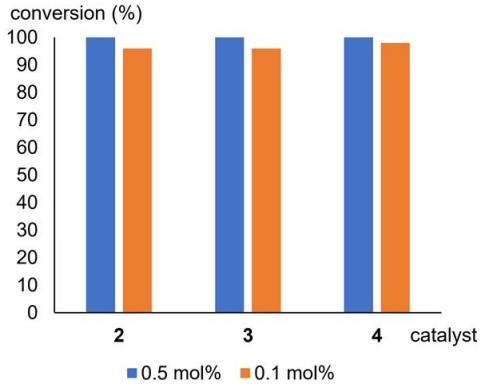


Figure 4. The conversion (%) of triethoxysilane in presence of 0.5 and 0.1 mol% of **2**–**4**.

The research results showed excellent catalytic activities of the cyclometalated platinum(II) complexes bearing eugenol, **1**–**4**, for hydrosilylation reaction with the triethoxy-group under mild conditions. Remarkably, complexes **1**–**4** exhibited better catalytic activities than many other Pt(II) complexes reported for hydrosilylation reactions of phenylacetylene by triethoxysilane [8–10]. For example, Afanasenko *et al.*, using 0.1 mol% of Pt(II) complex bearing acyclic diaminocarbenes as a catalyst in toluene, only 93% of triethoxysilane was converted to hydrosilylation products after 3 hours at 100 °C [10].

4. CONCLUSIONS

The structure of three complexes [PtCl(Eug)(amine)] (**2**–**4**) synthesized by the reactions between dinuclear complex Pt(μ-Cl)(Eug)]$_2$ (**1**) with pyridine, 4-methylpyridine and quinoline respectively, was determined by ^{13}C NMR spectroscopy. The results showed that Eug coordinates with Pt *via* the C=C bond in the η^2 type. Moreover, complex **3** in solvent $CDCl_3$ exists in two structures due to the formation of hydrogen and halogen bonds with the solvent. Complexes **1**–**4** exhibit good catalytic activities at 70 ^{o}C without solvent and any other additives under air for 2 hours. In the presence of 0.5 mol% of catalysts, the triethoxysilane is completely converted to two hydrosilylation products, namely, (*E*)-triethoxy(styryl)silane) (β(*E*) – the major product) and (triethoxy(1-phenylvinyl)silane) (α – the minor product) with α/β(*E*) molar ratio ranging from 1:2.6 to 1:2.8. With only 0.1 mol% loading of complexes **2**–**4**, the conversion of triethoxysilane was slightly reduced with an efficiency of 97–99% under the same conditions.

Acknowledgements. This work was supported by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03-2019.15.

CRediT authorship contribution statement. PhamVan Thong: Investigation, Formal analysis, Writing manuscript. Dinh Ngoc Doan Trang: Investigation, Formal analysis. Truong Thuy Hang: Formal analysis. Nguyen Thi Thanh Chi: Methodology, Reviewing and Editing the manuscript, Supervision, Funding acquisition.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

1. Johnstone T. C., Suntharalingam K., Lippard S. J. - The next generation of platinum drugs: targeted Pt(II) agents, nanoparticle delivery, and Pt(IV) prodrugs, Chem. Rev, **116(5)** (2016) 3436–3486. https://doi.org/10.1021/acs.chemrev.5b00597.
2. Englinger B., Pirker C., Heffeter P., Terenzi A., Kowol C. R., Keppler B. K., Berger W. - Metal drugs and the anticancer immune response, Chem. Rev., **119(2)** (2019) 1519–1624. https://doi.org/10.1021/acs.chemrev.8b00396.
3. Labinger J. A. - Platinum-catalyzed C–H functionalization, Chem. Rev., **117(13)** (2017) 8483–8496. https://doi.org/10.1021/acs.chemrev.6b00583.
4. Lukin R. Y., Kuchkaev A. M., Sukhov A. V., Bekmukhamedov G. E., D Yakhvarov. G. - Platinum-catalyzed hydrosilylation in polymer chemistry, Polymers, **12(10)** (2020) 2174. https://doi.org/10.3390/polym12102174.
5. Zhang F., Bai Y., Yang X., Li J., Peng J. - *N*-heterocyclic carbene platinum complexes functionalized with a polyether chain and silyl group: Synthesis and application as a

catalyst for hydrosilylation, Phosphorus, Sulfur, and Silicon and the Related Elements, **192(12)** (2017) 1271–1278. https://doi.org/10.1080/10426507.2017.1321647.

6. Walczak A., Stachowiak H., Kurpik G., Kaźmierczak J., Hreczycho G., Stefankiewicz A. R. - High catalytic activity and selectivity in hydrosilylation of new Pt(II) metallosupramolecular complexes based on ambidentate ligands, J. Catal., **373** (2019) 139–146. https://doi.org/10.1016/j.jcat.2019.03.041.
7. Nguyen V. H., Dang T. T., Nguyen H. H., Huynh H. V. - Platinum(II) 1,2,4-Triazolin-5-ylidene Complexes: Stereoelectronic Influences on Their Catalytic Activity in Hydroelementation Reactions, Organometallics, **39(12)** (2020) 2309–2319. https://doi.org/10.1021/acs.organomet.0c00260.
8. Naganawa Y., Maegawa Y., Guo H., Gholap S. S., Tanaka S., Sato K., Inagaki S., Nakajima Y. - Heterogeneous hydrosilylation reaction catalysed by platinum complexes immobilized on bipyridine-periodic mesoporous organosilicas, Dalton Trans., **48** (17) (2019) 5534–5540. https://doi.org/10.1039/C9DT00078J.
9. Fotie J., Agbo M. E., Qu F., Tolar T. - Dichloro(ethylenediamine)platinum(II), a water-soluble analog of the antitumor cisplatin, as a heterogeneous catalyst for a stereoselective hydrosilylation of alkynes under neat conditions, Tetrahedron Lett., **61** (36) (2020) 152300. https://doi.org/10.1016/j.tetlet.2020.152300.
10. Afanasenko A. M., Chulkova T. G., Boyarskaya I. A., Islamova R. M., Legin A. A., Keppler B. K., Selivanov S. I., Vereshchagin A. N., Elinson M. N., Haukka M. - *C,N*-chelated diaminocarbene platinum(II) complexes derived from 3,4-diaryl-1H-pyrrol-2,5-diimines and *cis*-dichlorobis(isonitrile)platinum(II): Synthesis, cytotoxicity, and catalytic activity in hydrosilylation reactions, J. Organomet. Chem., **923** (2020) 121435. https://doi.org/10.1016/j.jorganchem.2020.121435.
11. Dobrynin M. V., Kasatkina S. O., Baykov S. V., Savko P. Y., Antonov N. S., Mikherdov A. S., Boyarskiy V. P., Islamova R. M. - Cyclometallated Platinum(II) Complexes for Obtaining Phenyl-Containing Silicone Rubbers via Catalytic Hydrosilylation Reaction, Russian Journal of General Chemistry, **92(1)** (2022) 79–84. https://doi.org/10.1134/S107036322201011X.
12. Chi N. T. T., Da T. T., Robeyns K., Meervelt L. V., Mai T. T. C., Dat N. D., Dinh N. H. - Synthesis, crystal and solution structures of platinacyclic complexes containing eugenol, the main bioactive constituent of *Ocimum sanctum L.* oil, Polyhedron, **151** (2018) 330–337. https://doi.org/10.1016/j.poly.2018.05.055.
13. Hang T. T., Chi N. T. T. - ^{1}H NMR spectra of a series of complexes [PtCl(eugenol-1H)(amine)](amine: pyridin, 4-Me-pyridin, quinolin, *p*-cloanilin, *p*-toluidin), Vietnam Journal of Science and Technology - MOST, **62(3)** (2020) 1–3.
14. Jun C. H., Crabtree R. H. - Dehydrogenative silation, isomerization and the control of *syn*- vs. *anti*-addition in the hydrosilation of alkynes, J. Organomet. Chem., **447(2)** (1993) 177–187. https://doi.org/10.1016/0022-328X(93)80236-5.
15. Chi N. T. T., Da T. T., Ha N. V., Dinh N. H. - Synthesis and spectral characterization of platinum(II) complexes containing eugenol, a natural allylphenol, J. Coord. Chem., **70(6)** (2017) 1008–1019. https://doi.org/10.1080/00958972.2017.1281917.