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Study on the anti-sulfur-poisoning characteristics of platinum–acetylide–phosphine complexes as catalysts for hydrosilylation reactions

Jiayun Li, Congbai Niu, Jiajian Peng*, Yuan Deng, Guodong Zhang, Ying Bai, Chao Ma, Wenjun Xiao and Guoqiao Lai

A series of platinum–acetylide–phosphine complexes were synthesized and their anti-sulfur-poisoning characteristics investigated. In comparison with Speier's and Karstedt's catalysts, the platinum–acetylide–phosphine complexes exhibited both higher catalytic activity and selectivity for the β-adduct for the hydrosilylation reactions under the same conditions. Furthermore, the complexes also exhibited a strong ability to resist to sulfur-poisoning. This indicated that the alkyne ligands containing the silyl group had a strong impact on the hydrosilylation reaction. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: platinum–acetylide–phosphine complexes; anti-sulfur poisoning; hydrosilylation

Introduction

A number of organosilicon monomers and polymers containing functional groups have been synthesized via hydrosilylation reactions. Hydrosilylation of C=C is one of the most important Si—C bond formation reactions and commercial reactions. Various transition metal catalysts have been successively researched and applied to the hydrosilylation reaction. In 1947, $H_2PtCl_6.6H_2O$/isopropanol (Speier's catalyst) was first found to be effective in the hydrosilylation of alkenes and alkynes with silanes.[1–3] Thereafter, Pt(0)–divinyltetramethyldisiloxane complex (Karstedt's catalyst), by virtue of its higher activity, gradually replaced Speier's catalyst.[4–8] For hydrosilylation of alkenes and alkynes with silanes Karstedt's catalyst is the most active catalyst in current use. However, sulfur compounds are still a poison for the platinum catalyst, and significantly decreased the catalytic activity of platinum catalysts for hydrosilylation processes. Usually, low catalytic activity of Karstedt's catalyst or Speier's catalyst was observed, owing to the raw material with trace amounts of sulfur, nitrogen and other elements in practical application, in particular sulfur element. Several of compounds, e.g. aluminum acetylacetonate, iron chelate complexes, as well as polyhydrosiloxane coat, have been reported to serve as anti-sulfur-poisoning agents of Pt catalyst.[9,10] Hence the development of new catalysts for the hydrosilylation reaction along with a strong ability to resist sulfur poisoning is an ongoing challenge. For example, *trans*-$Pt(PPh_3)_2[C{\equiv}CC_6H_6(OH)]_2$ has shown stable and high activity for addition-cross-linking curable; however, the reaction time was too long and still not satisfactory.[11–14] On the other hand, Soeda[11] found that *trans*-$Pt(PPh_3)_2[C{\equiv}CC_6H_5]_2$ showed catalytic activity of hydrosilylation in the presence of a small amount of poisonous sulfur. In this paper, a series of novel platinum–acetylide–phosphine complexes was synthesized, and tolerance to sulfur poisoning was investigated by catalytic hydrosilylation of styrene with triethoxysilane as a model reaction (Scheme 1).[15–19]

Experimental

General Information

All chemicals were purchased from Aldrich and were used as received. All synthesis procedures were carried out under argon using standard Schlenk and vacuum-line techniques. Solvents for synthesis were dried and degassed by standard methods before use.

Gas chromatography: Trace DSQ GC column DB-5 30 m × 2.5 mm × 0.25 mm, split 50:1, flow 1 mL min^{-1} constant flow, inlet temperature 260°C, column temperature 50°C (hold 1 min) then 15°C min^{-1} up to 260°C (hold 10 min).

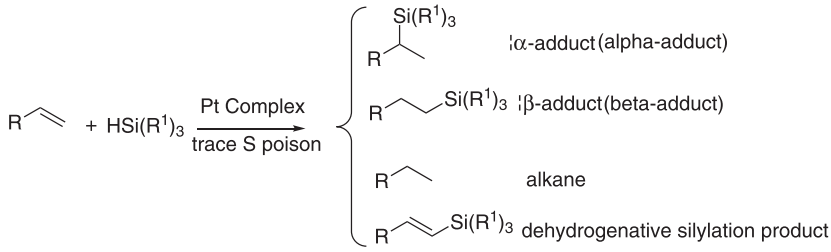
^1H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were measured using a Bruker Avance 400 MHz spectrometer operating at 400.13, 100.62, 79.49 and 161.97 MHz, respectively, using TMS as an internal standard and $CDCl_3$ as solvent. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 external standard.

Elemental analyses were performed on a Vario EL-III elemental analyzer, and IR spectra were recorded on a Nicolet 5700 instrument. GC-MS was tested with a Trace DSQ GC-MS column.

Speier's catalyst and Karstedt's catalyst were prepared by literature methods.[20]

* *Correspondence to: Jiajian Peng, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, People's Republic of China. E-mail: jjpeng@hznu.edu.cn*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, People's Republic of China



Scheme 1. Hydrosilylation of alkenes with triethoxysilane or triethylsilane. R^1: OEt, Et.

General Procedure for Synthesis of Platinum–Acetylide–Phosphine Complexes (Scheme 2)

Synthesis of trans-Pt(PPh$_3$)$_2$Cl$_2$, trans-Pt[PPh$_2$Si(CH$_3$)$_3$]$_2$Cl$_2$ and trans-Pt(PPh$_3$)$_2$(—C≡CPh)$_2$

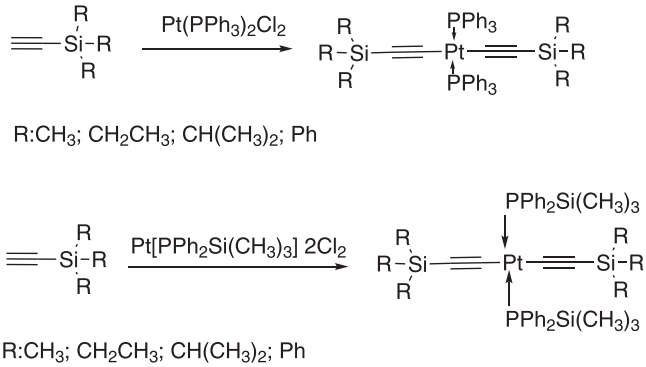
trans-Pt(PPh$_3$)$_2$Cl$_2$ (**1a**) was prepared by literature methods.[20]

trans-Pt[PPh$_2$Si(CH$_3$)$_3$]$_2$Cl$_2$ (**2a**): an excess of PPh$_2$Si(CH$_3$)$_3$ (2.5 mmol) was added to a boiling solution of CH$_3$OH (60 ml). K$_2$PtCl$_4$ (1 mmol) was added in water and the mixture was stirred at 60°C for 2 h. The solid was obtained by filtration and washed with water, CH$_3$OH and ethyl ether, respectively. The product was dried *in vacuo* to obtain **2a** in 87% yield (flavescent solid). ^{1}H NMR δ (ppm): 0.33 (s, 18H, Si(C*H*$_3$)$_3$), 7.10–7.58 (m, 20H, P*Ph*$_2$).^{13}C NMR δ (ppm): 0.10 (Si(*C*H$_3$)$_3$), 127.41 (t, $J_{C—P}$ = 6 Hz, meta), 129.40 (m, *ortho*), 132.10 (*para*), 135.13 (m, *ipso*) (P*Ph*$_3$). ^{29}Si NMR δ (ppm): 6.70. ^{31}P NMR δ (ppm): 31.60 ($J_{P—Pt}$ = 2618 Hz). Anal. Calcd for **2a** ($C_{30}H_{38}Cl_2P_2PtSi_2$): C, 46.03; H, 4.89. Found: C, 46.01; H, 4.88.

trans-Pt(PPh$_3$)$_2$(—C≡CPh)$_2$ (**3a**) (flavescent solid, 74 % yield) was prepared by literature methods. The spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR) and elemental analysis data of the prepared compound **3a** were in agreement with the assigned structures and with those found in the literature (Fig. 1).[21]

trans-Pt(PPh$_3$)$_2$[—C≡CC(CH$_3$)$_2$OH]$_2$ (**4a**) (yield 89%) was prepared by literature methods. Spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR) and elemental analysis data of the prepared compound **4a** were in agreement with the assigned structures and with those found in the literature.[21]

trans-Pt(PPh$_3$)$_2$[—C≡C(C$_6$H$_{10}$)OH]$_2$ (**5a**) (yield 91%) was prepared by literature methods. Spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{31}P NMR and IR) and elemental analysis data of the prepared compound **5a** were in agreement with the assigned structures and with those found in the literature.[21]



Scheme 2. Synthesis of *trans*-Pt(PPh$_3$)$_2$(—C≡C—SiR$_3$)$_2$ and *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$] $_2$(—C≡C-SiR$_3$)$_2$.

Synthesis of trans-Pt(PPh$_3$)$_2$(—C≡C—SiR$_3$)$_2$ and trans-Pt[PPh$_2$Si(CH$_3$)$_3$] $_2$(—C≡C—SiR$_3$)$_2$, R = —CH$_3$, —C$_2$H$_5$, —CH(CH$_3$)$_2$, —Ph

Synthesis of trans-Pt(PPh$_3$)$_2$(—C≡C—SiR$_3$)$_2$ R = —CH$_3$, —C$_2$H$_5$, —CH(CH$_3$)$_2$, —Ph. A mixture of *trans*-Pt(PPh$_3$)$_2$Cl$_2$ (1 mmol) and CH≡CSiR$_3$ (2.2 mmol) in diethylamine/THF (10 mmol/20 ml) was allowed to react in the presence of CuI (5 mg) at 80°C for 6 h. Evaporation of the solvent and purification of the residue by chromatography on alumina eluting with hexane–benzene (1:1) afforded the product. Recrystallization from *n*-hexane gave product *trans*-Pt(PPh$_3$)$_2$ (—C≡C—SiR$_3$)$_2$.

Complex **1b**: *trans*-Pt(PPh$_3$)$_2$ [CH≡CSi(CH$_3$)$_3$]$_2$ (flavescent solid, yield 91%), IR (KBr): 2087 cm^{-1} ($\nu_{C≡C}$). ^{1}H NMR δ (ppm): 0.02 (s, 18H, Si(*CH*$_3$)$_3$), 7.35–7.58 (m, 30H, P*Ph*$_2$).^{13}C NMR δ (ppm): −0.90 (Si(CH$_3$)$_3$), 104.71 (C—*C*≡C), 115.32 (t, J = 16.1 Hz, Pt—*C*≡C), 127.61 (t, $J_{C—P}$ = 6 Hz, meta), 129.10 (m, *ortho*), 133.81 (*para*), 135.90 (m, *ipso*) (P*Ph*$_3$). ^{29}Si NMR δ (ppm): 14.21. ^{31}P NMR δ (ppm): 18.60 ($J_{P—Pt}$ = 1837 Hz). Anal. Calcd for **1b** ($C_{46}H_{48}P_2Pt\ Si_2$): C, 60.44; H, 5.29. Found: C, 60.42; H, 5.28.

Complex **2b**: *trans*-Pt(PPh$_3$)$_2$[CH≡CSi(CH$_2$CH$_3$)$_3$]$_2$ (flavescent solid, yield 84%), IR (KBr): 2094 cm^{-1} ($\nu_{C≡C}$).^{1}H NMR δ (ppm): 0.64 (q, J = 12 Hz, 12H, Si(*CH*$_2$CH$_3$)$_3$), 1.04 (t, J = 12 Hz, 18H, Si(CH$_2$*CH*$_3$)$_3$), 7.30–7.72 (m, 30H, P*Ph*$_2$). ^{13}C NMR δ (ppm): 4.50 (Si (CH$_2$CH$_3$)$_3$), 7.51 (Si (CH$_2$CH$_3$)$_3$), 105.20 (C—*C*≡C), 121.51 (t, J = 16.1 Hz, Pt—*C*≡C), 127.92 (t, $J_{C—P}$ = 6 Hz, *meta*), 131.94 (m, *ortho*), 132.10 (*para*), 135.23 (m, *ipso*) (P*Ph*$_3$). ^{29}Si NMR δ (ppm): 16.10. ^{31}P NMR δ (ppm): 19.00 ($J_{P—Pt}$ = 1858 Hz). Anal. Calcd for **2b** ($C_{52}H_{60}P_2Pt\ Si_2$): C, 62.57; H, 6.06. Found: C, 62.55; H, 6.05.

Complex **3b**: spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, ^{31}P NMR and IR) and elemental analysis data of the prepared compound **3b** were in agreement with the assigned structures and with those found in the literature.[21] Complex **4b**: *trans*-Pt(PPh$_3$)$_2$ (CH≡CSiPh$_3$)$_2$ (flavescent solid, yield 79%), IR (KBr): 2108 cm^{-1} ($\nu_{C≡C}$).^{1}H NMR δ (ppm): 6.98–7.71 (m, 60H, P*Ph*$_2$, Si (*Ph*)$_3$). ^{13}C NMR δ (ppm): 102.11 (C—*C*≡C), 112.51 (t, J = 15 Hz, Pt—*C*≡C), 127.72 (t, $J_{C—P}$ = 6 Hz, *meta*) , 131.92 (m, *ortho*), 134.71 (*para*), 135.52 (m, *ipso*) (P*Ph*$_3$), 129.73 (t, J = 6 Hz, *meta*), 132.14 (m, *ortho*), 134.91 (*para*), 136.11 (m, *ipso*) (Si*Ph*$_3$). ^{29}Si NMR δ (ppm): −15.20. ^{31}P NMR δ (ppm): 19.20 ($J_{P—Pt}$ = 1818 Hz). Anal. Calcd for **4b** ($C_{76}H_{60}P_2Pt\ Si_2$): C, 70.95; H, 4.70. Found: C, 70.97; H, 4.70.

Synthesis of trans-Pt[PPh$_2$Si(CH$_3$)$_3$] $_2$(≡C—C—SiR$_3$)$_2$, R = —CH$_3$, —C$_2$H$_5$, —CH(CH$_3$)$_2$, —Ph. A mixture of *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$] $_2$Cl$_2$ (1 mmol) and CH≡CSiR$_3$ (R = —CH$_3$, —C$_2$H$_5$, —CH(CH$_3$)$_2$, —Ph) (2.2 mmol) in diethylamine/THF was allowed to react in the presence of CuI (5 mg) at 80°C for 6 h. Evaporation of the solvent and purification of the residue by chromatography on alumina eluting with hexane/benzene (1:1) afforded the product. Recrystallization from *n*-hexane gave product *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$] $_2$(—C≡C—SiR$_3$)$_2$.

Complex **5b**: *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$]$_2$[CH≡CSi(CH$_3$)$_3$]$_2$ (flavescent solid, yield 84%), IR (KBr): 2033 cm^{-1} ($\nu_{C≡C}$). ^{1}H NMR δ (ppm): 0.02 (s, 18H, Si(*CH*$_3$)$_3$), 0.12 (s, 18H, Si(*CH*$_3$)$_3$), 7.10–7.76 (m, 20H, P*Ph*$_2$).^{13}C NMR δ (ppm): 1.40 (Si(*CH*$_3$)$_3$), 1.90 (Si(*CH*$_3$)$_3$), 102.91 (C—*C*≡C),

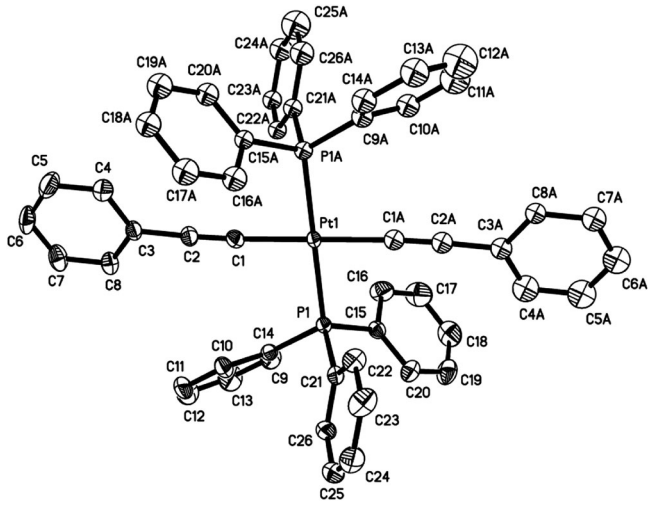


Figure 1. Molecular structure of **3a** drawn with 30% probability displacement ellipsoids.

118.62 (t, $J = 15$ Hz, Pt—*C*≡C), 128.40 (t, $J_{C—P} = 8$ Hz, *meta*), 129.81 (m, *ortho*), 131.80 (*para*), 132.01 (m, *ipso*) (P*Ph*$_3$). ^{29}Si NMR δ (ppm): 6.90, 14.21. ^{31}P NMR δ (ppm): 31.60 ($J_{P—Pt} = 2898$ Hz). Anal. Calcd for **5b** ($C_{40}H_{56}P_2Pt\ Si_4$): C, 53.01; H, 6.23. Found: C 52.99; H 6.21.

Complex **6b**: *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$]$_2$[CH≡CSi(CH$_2$CH$_3$)$_3$]$_2$ (flavescent solid, yield 81%), IR (KBr): 2073 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR δ (ppm): 0.01 (s, 18H, Si(*CH*$_3$)$_3$), 0.54 (q, $J = 12$ Hz, 12H, Si(*CH*$_2$CH$_3$)$_3$), 0.93 (t, $J = 12$ Hz, 18H, Si(CH$_2$*CH*$_3$)$_3$), 6.90–7.73 (m, 20H, P*Ph*$_2$).^{13}C NMR δ (ppm): 0.10 (Si(*CH*$_3$)$_3$), 4.60 (Si (CH$_2$*CH*$_3$)$_3$), 7.51 (Si (*CH*$_2$CH$_3$)$_3$), 110.31 (C—*C*≡C), 125.22 (t, $J = 15$ Hz, Pt—*C*≡C), 127.31 (t, $J_{C—P} = 8$ Hz, *meta*), 129.5 (m, *ortho*), 131.13 (*para*), 132.11 (m, *ipso*) (P*Ph*$_3$). ^{29}Si NMR δ (ppm): 7.10, 16.50. ^{31}P NMR (CDCl$_3$, 162 MHz) δ (ppm): 31.60 ($J_{P—Pt} = 2818$ Hz). Anal. Calcd for **6b** ($C_{46}H_{68}P_2Pt\ Si_4$): C 55.78; H 6.92. Found: C 55.80; H 6.92.

Complex **7b**: *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$]$_2$[CH≡CSi(CH(CH$_3$)$_2$)$_3$]$_2$ (flavescent solid, yield 83%), IR (KBr): 2068 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR δ (ppm): 0.01 (s, 18H, Si(*CH*$_3$)$_3$), 0.35 (septet, $J = 7.3$ Hz, 6H, *CH*(CH$_3$)$_2$), 0.61 (d, $J = 7.3$ Hz, 36H, CH(*CH*$_3$)$_2$), 7.08–7.81 (m, 20H, P*Ph*$_2$). ^{13}C NMR δ (ppm): −0.03 (Si(*CH*$_3$)$_3$), 10.90 (*CH*(CH$_3$)$_2$), 18.41 (CH(*CH*$_3$)$_2$), 94.92 (C—*C*≡C), 124.13 (t, $J = 15$ Hz, Pt—*C*≡C), 127.31 (t, $J_{C—P} = 8$ Hz, *meta*), 129.92 (m, *ortho*), 131.84 (*para*), 132.41 (m, *ipso*) (P*Ph*$_3$). ^{29}Si NMR δ (ppm): 6.80, 18.10. ^{31}P NMR δ (ppm): 30.60 ($J_{P—Pt} = 2834$ Hz). Anal. Calcd for **7b** ($C_{52}H_{80}P_2Pt\ Si_4$): C, 58.12; H, 7.50. Found: C 58.10; H 7.51.

Complex **8b**: *trans*-Pt[PPh$_2$Si(CH$_3$)$_3$]$_2$(CH≡CSiPh$_3$)$_2$ (flavescent solid, yield 73%), IR (KBr): 2127 cm^{-1} ($\nu_{C\equiv C}$). ^{1}H NMR δ (ppm): 0.08 (s, 18H, Si(*CH*$_3$)$_3$), 6.90–8.02 (m, 50H, P*Ph*$_2$, Si (*Ph*)$_3$).^{13}C NMR δ (ppm): 1.00 (Si(CH$_3$)$_3$), 102.51 (C—*C*≡C), 118.82 (t, $J = 15$ Hz, Pt—*C*≡C), 127.81 (t, $J_{C—P} = 6$ Hz, meta) , 130.10 (m, *ortho*), 132.01 (*para*), 134.73 (m, *ipso*) (P*Ph*$_3$), 129.11 (t, $J = 6$ Hz, *meta*), 131.31 (m, *ortho*), 132.22 (*para*), 134.93 (m, *ipso*) (Si*Ph*$_3$). ^{29}Si NMR δ (ppm): 7.10, −15.60. ^{31}P NMR δ (ppm): 31.80 ($J_{P—Pt} = 2818$ Hz). Anal. Calcd for **8b** ($C_{70}H_{68}P_2Pt\ Si_4$): C 65.75; H 5.36. Found: C 65.73; H 5.37.

Hydrosilylation

Typical hydrosilylation reaction procedures were as follows. A given amount of the alkene and silane was added to a 10 ml round-bottomed flask equipped with a magnetic stirrer and a given amount of catalyst was added. This mixture was heated to the appropriate temperature and the hydrosilylation reaction was allowed to proceed with constant stirring for 2 h. At the end of the reaction, the conversion of alkene and the selectivity were determined by GC. All data in the tables are the average values of three experiments.

Hydrosilylation of styrene with triethoxysilane: β-Adduct [triethoxy (phenylethyl)silane] and α-adduct [triethoxy(1-phenylethyl)silane]. Spectroscopic data (^{1}H NMR) and elemental analysis data of the prepared compounds were in agreement with the assigned structures and with those found in the literature.[22]

Hydrosilylation of o-methylstyrene with triethoxysilane

β-Adduct [triethoxy(*o*-methylphenylethyl)silane]: ^{1}H NMR δ (ppm): 1.05 (t, $J = 8.5$ Hz, 2H, Si—CH$_2$), 1.37 (t, $J = 7.0$ Hz, 9H, CH$_3$), 2.42 (s, 3H, CH$_3$), 2.77 (t, $J = 8.5$ Hz, 2H, CH$_2$), 3.87 (q, $J = 7.0$ Hz, 6H, O—CH$_2$), 7.08–7.35 (m, 4H, Ph). ^{13}C NMR δ (ppm): 142.77 (*ipso*, CH$_2$CH$_2$*Ph*), 135.32 (*ipso*), 130.11 (*ortho*), 128.06 (*meta*), 126.11 (*meta*), 125.82 (*para*) (CH$_3$*Ph*), 58.40 (OCH$_2$CH$_3$), 26.34 (CH$_2$*CH*$_2$Ph), 19.07 (*CH*$_3$Ph), 18.36 (OCH$_2$*CH*$_3$), 11.53 (SiCH$_2$). ^{29}Si NMR δ (ppm): −46.09. MS (EI) *m/z* (%): 283 (M$^+$, 16), 282 (100). Anal. Calcd for [triethoxy(*o*-methylphenylethyl)silane] ($C_{15}H_{26}O_3Si$): C 63.78; H 9.28; O 16.99. Found: C 63.75; H 9.27; O 17.00. IR (KBr): 449, 632, 764, 784, 969, 1015, 1415, 2766, 2930 cm^{-1}.

Hydrosilylation of m-methylstyrene with triethoxysilane

β-Adduct [triethoxy(*m*-methylphenylethyl)silane]: ^{1}H NMR δ (ppm): 1.10 (t, $J = 8.5$ Hz, 2H, Si—CH$_2$), 1.36 (t, $J = 7.0$ Hz, 9H, CH$_3$), 2.43 (s, 3H, CH$_3$), 2.79 (t, $J = 8.5$ Hz, 2H, CH$_2$), 3.94 (q, $J = 7.0$ Hz, 6H, O—CH$_2$), 7.15–7.22 (m, 4H, Ph). ^{13}C NMR δ (ppm): 144.60 (*ipso*, CH$_2$CH$_2$*Ph*), 137.59 (*ipso*), 128.65 (*ortho*), 128.27 (*meta*), 126.38 (*ortho*), 124.91 (*para*) (CH$_3$*Ph*), 58.33 (OCH$_2$CH$_3$), 28.99 (CH$_2$*CH*$_2$Ph), 21.32 (CH$_3$Ph), 18.34 (OCH$_2$*CH*$_3$), 12.85 (SiCH$_2$). ^{29}Si NMR δ (ppm): −46.24. MS (EI) *m/z* (%): 283 (M$^+$, 15), 282 (100). Anal. Calcd for [triethoxy(*m*-methylphenylethyl)silane] ($C_{15}H_{26}O_3Si$): C 63.78; H 9.28; O 16.99. Found: C 63.77; H 9.28; O 16.98. IR (KBr): 457, 637, 715, 743, 767, 971, 1017, 1417, 2810, 3042 cm^{-1}.

Hydrosilylation of p-methylstyrene with triethoxysilane

β-Adduct [triethoxy(*p*-methylphenylethyl)silane]: ^{1}H NMR δ (ppm): 1.03 (t, $J = 8.5$ Hz, 2H, Si—CH$_2$), 1.28 (t, $J = 7.0$ Hz, 9H, CH$_3$), 2.31 (s, 3H, CH$_3$), 2.70 (t, $J = 8.5$ Hz, 2H, CH$_2$), 3.87 (q, $J = 7.0$ Hz, 6H, O—CH$_2$), 7.07–7.11 (m, 4H, Ph). ^{13}C NMR δ (ppm): 141.66 (*ipso*, CH$_2$CH$_2$*Ph*), 134.97 (*ipso*), 129.02 (*ortho*), 127.82 (*meta*) (*Ph*), 58.80 (OCH$_2$CH$_3$), 28.53 (CH$_2$*CH*$_2$Ph), 20.96 (*CH*$_3$Ph), 18.12 (OCH$_2$*CH*$_3$), 12.08 (SiCH$_2$). ^{29}Si NMR δ (ppm): −45.96. MS (EI) *m/z* (%): 283 (M$^+$, 16), 282 (100). Anal. Calcd for [triethoxy(*p*-methylphenethyl)silane] ($C_{15}H_{26}O_3Si$): C 63.78; H 9.28; O 16.99. Found: C 63.79; H 9.27; O 16.99. IR (KBr): 453, 631, 767, 857, 971, 1019, 1411, 2768, 3231 cm^{-1}.

Hydrosilylation of p-methoxystyrene with triethoxysilane

β-Adduct [triethoxy(*p*-methoxyphenylethyl)silane]: ^{1}H NMR δ (ppm): 1.02 (t, $J = 8.5$ Hz, 2H, Si—CH$_2$), 1.24 (t, $J = 7.0$ Hz, 9H, CH$_3$), 2.70 (t, $J = 8.5$ Hz, 2H, CH$_2$), 3.70 (s, 3H, O—CH$_3$), 3.79 (q, $J = 7.0$ Hz, 6H, O—CH$_2$), 6.95–7.26 (m, 4H, Ph). ^{13}C NMR δ (ppm): 157.79 (*ipso*, CH$_2$CH$_2$*Ph*), 136.57 (*ipso*), 128.58 (*meta*), 113.65 (*ortho*) (CH$_3$O*Ph*), 58.21 (OCH$_2$CH$_3$), 54.84(OCH$_3$), 28.05 (CH$_2$*CH*$_2$Ph), 18.23 (OCH$_2$*CH*$_3$), 12.92 (SiCH$_2$). ^{29}Si NMR (CDCl$_3$) δ (ppm): −46.29. MS (EI) *m/z* (%): 299 (M$^+$, 22), 298 (100). Anal. Calcd for [triethoxy(*p*-methoxyphenylethyl)silane] ($C_{15}H_{26}O_4Si$): C 60.37; H 8.78; O 21.44. Found: C 60.35; H 8.78; O 21.45. IR (KBr): 467, 637, 781, 857, 964, 1085, 1483, 2884, 3222 cm^{-1}.

Hydrosilylation of p-fluorostyrene with triethoxysilane

β-Adduct [triethoxy(*p*-fluorophenylethyl)silane]: ^{1}H NMR δ (ppm): 1.01 (t, J = 8.5 Hz, 2H, Si—CH_2), 1.21 (t, J = 7.0 Hz, 9H, CH_3), 2.70 (t, J = 8.5 Hz, 2H, CH_2), 3.78 (q, J = 7.0 Hz, 6H, O—CH_2), 6.84–7.24 (m, 4H, Ph). ^{13}C NMR δ (ppm): 162.36 (s, $^{1}J_{C—F}$ = 241 Hz, *para*), 139.65 (d, $^{4}J_{C—F}$ = 3.0 Hz, *ipso*), 129.04 (d, $^{3}J_{C—F}$ = 6.0 Hz, *ortho*), 114.72 (d, $^{2}J_{C—F}$ = 21 Hz, *meta*) (F*Ph*), 58.29 (OCH_2CH_3), 28.15 (CH_2CH_2Ph), 18.17 (OCH_2CH_3), 12.76 ($SiCH_2$). ^{29}Si NMR δ (ppm): −46.55. MS (EI) *m/z* (%): 287 (M^+, 20), 286 (100). Anal. Calcd for [triethoxy(*p*-fluorophenylethyl)silane] ($C_{14}H_{23}FO_3Si$): C 58.71; H 8.09; O 16.76. Found: C 58.83; H 8.08; O 16.77. IR (KBr): 449, 467, 638, 783, 859, 974, 1089, 1485, 2993, 3429 cm^{-1}.

Hydrosilylation of 1-hexene with triethoxysilane: β-Adduct [triethoxy(hexyl)silane]. Spectroscopic data (^{1}H NMR ^{13}C NMR and ^{29}Si NMR) and elemental analysis data of the prepared compound were in agreement with the assigned structures and with those found in the literature.[22]

Hydrosilylation of 1-dodecene with triethoxysilane: β-Adduct [triethoxy(dodecyl)silane] . Spectroscopic data (^{1}H NMR ^{13}C NMR and ^{29}Si NMR) and elemental analysis data of the prepared compound were in agreement with the assigned structures and with those found in the literature.[22]

Hydrosilylation reaction of styrene with triethylsilane: β-Adduct [triethyl(phenylethyl)silane]. Spectroscopic data (^{1}H NMR ^{13}C NMR and ^{29}Si NMR) and elemental analysis data of the prepared compound were in agreement with the assigned structures and with those found in the literature.[22]

Study of the Anti-Sulfur-Poisoning Characteristics of the Synthesized Platinum–Acetylide–Phosphine Complexes

A given amount of the alkene, silane and benzothiazole as sulfur poisoning was added to a 10 ml round-bottomed flask equipped with a magnetic stirrer and a given amount of catalyst was then added. This mixture was heated to the appropriate temperature and the hydrosilylation reaction was allowed to proceed with constant stirring for 2 h. At the end of the reaction, the conversion of alkene and the selectivity was determined by GC.

X-Ray Structure Determinations of Complexes 3a

Colorless single crystals of the compounds (dimensions, **3a**: 0.35 × 0.31 × 0.30 mm) were produced by slow evaporation of the solvents from solutions in hexane–dichloromethane mixtures at 25°C. Diffraction data were collected at room temperature by the φ-scan and ω-scan technique on a Smart Apex Duo diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXTL-PLUS)[23] and subsequently difference Fourier synthesis, and were then refined by full-matrix least squares on F^2 (SHELXL-97).[24] Absorption correction types were carried out using a multi-scan method. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically idealized positions. Crystal data and details of the structures are given in Table 1.

Table 1. Crystal data, data collection, and structure refinement details

	3a·2CHCl$_3$
Empirical formula	$C_{54}H_{42}Cl_6P_2Pt$
Formula weight	1160.61
Crystal system	Triclinic
space group	P-1
Unit cell dimensions	
a (Å)	8.2677(5)
b (Å)	12.0185(7)
c (Å)	12.9515(8)
α (°)	83.0290(10)
β (°)	84.5930(10)
γ (°)	82.4900(10)
Volume (Å^3)	1262.44(13)
Z, calculated density	1, 1.527 Mg m^{-3}
Abs. coeff. (mm^{-1})	3.195
F(000)	576
Reflections collected/unique	14 845/4368 [*R*(int) = 0.0206]
Goodness-of-fit on F^2	1.123
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0253, wR_2 = 0.0783
R indices (all data)	R_1 = 0.0321, wR_2 = 0.1135

Results and Discussion

Platinum acetylide complexes such as **3a** are readily prepared in high yields from the reaction of phenylacetylene with *trans*-$(PPh_3P)_2PtCl_2$.[25–29] Complexes **4a** and **5a** are also prepared in high yields.[25–29] In this paper, *trans*-platinum acetylide complexes (**1b–4b**) were synthesized as shown in Scheme 2. *trans*-$Pt[PPh_2Si(CH_3)_3]_2Cl_2$ **2a** was synthesized from K_2PtCl_4 and $PPh_2Si(CH_3)_3$. A series of novel platinum–acetylide–phosphine complexes **5b–8b** was synthesized. The appropriate alkyne-containing silyl group was added to a degassing and a dehydrating solution of *trans*-$Pt[PPh_2Si(CH_3)_3]_2Cl_2$ in Et_2NH–THF. A catalytic amount of CuI was added and the mixture was stirred at 80°C for 6 h. After work-up, the *trans*-$(PPh_3)_2Pt(C{\equiv}CSiR_3)_2$ complexes, **5b–8b**, were all isolated as stable solids in good yield. Infrared spectroscopy is a useful tool to confirm the chemical modifications proposed. The bands present in the diffuse-reflection infrared Fourier transform spectra of **1b** at 2087 cm^{-1}, **2b** at 2094 cm^{-1} … and **8b** at 2127 cm^{-1} are assigned to the presence of carbon–carbon triple bonds.[30–33] The structure of complex **3a** was determined by X-ray analysis (Figs. 1 and 2) and all of the platinum acetylide complexes were also characterized by

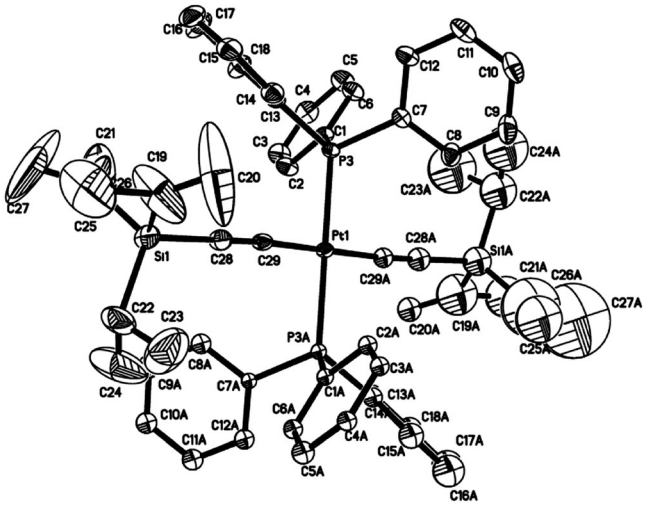


Figure 2. Molecular structure of **3b** drawn with 30% probability displacement ellipsoids.

NMR spectroscopy. All of the prepared complexes showed ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{29}Si NMR spectroscopic data in accordance with the proposed structures. Elemental analysis data and theoretical values for the platinum complexes **1a–8b** were also found to be in accordance. These results were obtained after the synthesis of a series of platinum acetylide complexes.

The platinum complexes prepared were tested in the hydrosilylation reaction of styrene with triethoxysilane as model reaction, and the results are listed in Table 2. At the same time, benzothiazole was added to the reaction mixtures to check the ability to resist sulfur poisoning of these prepared platinum acetylide complexes. The hydrosilylation reaction was performed by Speier's catalyst or Karstedt's catalyst with no sulfur compound, and showed a high level of conversion, but only a low level of β-adduct selectivity was obtained. The hydrosilylation reaction was examined using *trans*-$Pt(PPh_3)_2Cl_2$ or *trans*-$Pt[PPh_2Si(CH_3)_3]_2Cl_2$ as a catalyst under similar conditions; this showed a high level of conversion and β-adduct selectivity was obtained. No β-adduct was detected for $Pd(PPh_3)_2Cl_2$ catalyst. The role of PPh_3 or $(CH_3)_3SiPPh_2$ ligand was thought to improve the selectivity of the β-adduct.[34] However, Speier's catalyst or Karstedt's catalyst was inactive under hydrosilylation reaction conditions when a small amount of benzothiazole was added. A similar situation occurred when *trans*-$Pt(PPh_3)_2Cl_2$ or *trans*-$Pt[PPh_2Si(CH_3)_3]_2Cl_2$catalyst was used (Table 2, entries 1–11). Although a low level of catalytic activity and selectivity of β-adduct was observed in the hydrosilylation reaction of the styrene with triethoxysilane catalyzed with *trans*-$Pt(PPh_3)_2(—C{\equiv}CPh)_2$ (**3a**), **3a** exhibited tolerance to sulfur poisoning. *trans*-$Pt(PPh_3)_2[—C{\equiv}CC(CH_3)_2OH]_2$ (**4a**) and *trans*-$Pt(PPh_3)_2[—C{\equiv}C(C_6H_{10})OH]_2$ (**5a**) showed the same results as *trans*-$Pt(PPh_3)_2(—C{\equiv}CPh)_2$ (**3a**).

This prompted us to prepare a series of platinum acetylide complexes (**1b–8b**). In comparison with **3a**, when the hydrosilylation reaction was undertaken using a series of platinum–acetylide–phosphine complexes (**1b–8b**) as catalysts, both higher catalytic activity and selectivity for the β-adduct were exhibited. Although the catalytic activities of platinum–acetylide–phosphine complexes (**1b–4b; 5b–8b**) catalysts slightly decreased with increasing steric hindrances of the alkyne-containing silyl group, the selectivity of the β-adduct clearly increased. This demonstrated that the attached substituents of alkyne containing silyl group had a significant impact on the catalytic process, especially on the selectivity of the β-adduct. However, in comparison with **1b**, when the hydrosilylation reaction was undertaken by **5b** as the catalysts, the conversion of styrene decreased slightly, while the selectivities were constant. This demonstrated that the attached substituents of phosphine ligands had less impact on the catalytic process. At the same time, platinum–acetylide–phosphine complexes showed a strong ability to resist sulfur poisoning. Therefore, it can also be assumed that the alkyne ligands containing a silyl group offered a strong ability to resist sulfur poisoning and had a strong impact on the hydrosilylation reaction.

Although the conversion of styrene increased with increasing amounts of **4b** used, the selectivities were constant (Table 1, entries 35, 38 and 39). When the hydrosilylation reaction was undertaken using **4b** in the presence of trace amounts of poisonous sulfur, both the conversion of styrene and the selectivities were constant. Along with the amounts of sulfur poisoning increasing, the conversions of styrene decreased, while the selectivities remained constant.

Table 2. Results of the hydrosilylation reaction of styrene with triethoxysilane

Entry	Catalyst (mol %)	S poison (mol %)	Conversion (%)	Selectivity (%)		
				β	α	By-product[a]
1	Karstedt's 0.025	—	99.8	60.1	38.7	1.2
2	Karstedt's 0.025	0.02	—	—	—	—
3	Karstedt's 0.05	—	99.9	59.9	38.8	1.3
4	Karstedt's 0.05	0.02	—	—	—	—
5	Speier 0.05	—	85.7	65.6	34.1	0.3
6	Speier 0.05	0.02	—	—	—	—
7	$Pd(PPh_3)_2Cl_2$	—	4.74%	—	—	100
8	**1a** 0.05	—	95.4	82.9	13.7	3.4
9	**1a** 0.05	0.02	—	—	—	—
10	**2a** 0.05	—	94.7	83.8	13.1	3.1
11	**2a** 0.05	0.02	—	—	—	—
12	**3a** 0.05	—	64.7	74.7	12.9	12.4
13	**3a** 0.05	0.1	59.7	75.1	12.5	12.4
14	**4a** 0.05	—	41.7	65.7	19.9	14.4
15	**4a** 0.05	0.1	35.2	65.8	20.0	14.2
16	**5a** 0.05	—	33.9	61.2	28.4	10.4
17	**5a** 0.05	0.1	28.4	61.3	28.3	10.4
18	**1b** 0.05	—	92.1	91.2	6.0	2.8
19	**1b** 0.05	0.1	85.4	91.3	5.8	2.9
20	**2b** 0.05	—	91.4	91.8	5.1	3.1
21	**2b** 0.05	0.1	84.9	92.0	5.0	3.0
22	**3b** 0.05	—	90.9	93.4	3.3	3.3
23	**3b** 0.05	0.1	84.1	93.5	3.2	3.3
24	**5b** 0.05	—	90.7	91.9	5.7	2.4
25	**5b** 0.05	0.1	84.8	92.1	5.6	2.3
26	**6b** 0.05	—	90.1	91.9	5.1	3.0
27	**6b** 0.05	0.1	83.2	92.3	4.9	2.8
28	**7b** 0.05	—	89.9	93.6	3.3	3.1
29	**7b** 0.05	0.1	82.7	93.7	3.2	3.1
30	**8b** 0.05	—	89.8	95.1	1.2	3.7
31	**8b** 0.05	0.1	81.5	95.3	1.1	3.6
32	**4b** 0.05	—	90.2	94.8	1.3	3.9
33	**4b** 0.05	0.02	90.2	94.8	1.3	3.9
34	**4b** 0.05	0.05	90.1	94.7	1.3	4.0
35	**4b** 0.05	0.1	82.9	95.0	1.2	3.8
36	**4b** 0.05	0.2	71.9	95.2	1.1	3.7
37	**4b** 0.05	0.5	59.8	95.5	0.9	3.6
38	**4b** 0.025	0.1	78.2	95.2	1.1	3.7
39	**4b** 0.1	0.1	91.2	94.7	1.2	4.1

Reaction conditions: styrene 4.0 mmol; triethoxysilane 4.4 mmol; 90°C; 2 h.
Analyzed by GC-MS; S poison: benzothiazole; by-product: ethylbenzene; no unsaturated adduct.

1a: *trans*-$Pt(PPh_3)_2Cl_2$
2a: *trans*-$Pt[PPh_2Si(CH_3)_3]_2Cl_2$
3a: *trans*-$Pt(PPh_3)_2(C{\equiv}CPh)_2$
4a: *trans*-$Pt(PPh_3)_2[-C{\equiv}CC(CH_3)_2OH]_2$
5a: *trans*-$Pt(PPh_3)_2[-C{\equiv}C(C_6H_{10})OH]_2$
1b: *trans*-$Pt(PPh_3)_2(C{\equiv}CSiMe_3)_2$
2b: *trans*-$Pt(PPh_3)_2(C{\equiv}CSiEt_3)_2$
3b: *trans*-$Pt(PPh_3)_2\{C{\equiv}CSi[CH(CH_3)_2]_3\}_2$
4b: *trans*-$Pt(PPh_3)_2(C{\equiv}CSiPh_3)_2$
5b: *trans*-$Pt[PPh_2Si(CH_3)_3]_2[CH{\equiv}CSi\ (CH_3)_3]_2$
6b: *trans*-$Pt[PPh_2Si(CH_3)_3]_2[CH{\equiv}CSi\ (CH_2CH_3)_3]_2$
7b: *trans*-$Pt[PPh_2Si(CH_3)_3]_2[CH{\equiv}CSi\ (CH(CH_3)_2)_3]_2$
8b: *trans*-$Pt[PPh_2Si(CH_3)_3]_2(CH{\equiv}CSi\ Ph_3)_2$

Table 3. Results of the hydrosilylation reaction of aliphatic alkenes with triethoxysilane

Entry	Alkene	S poison (mol%)	Silane	Conv.	Selectivity (%)			
					β	α	Unsaturated	1-Ethylbenzene
1	2-Methylstyrene	—	Triethoxysilane	92.4	95.2	1.4	—	3.4
2		0.1		85.3	95.4	1.3	—	3.3
3	3-Methylstyrene	—		91.4	94.7	1.5	—	3.8
4		0.1		83.7	94.9	1.5	—	3.6
5	4-Methylstyrene	—		89.4	96.1	1.2	—	2.7
6		0.1		82.5	96.1	1.3	—	2.6
7	4-Methoxystyrene	—		93.4	95.4	1.5	—	3.1
8		0.1		86.1	95.6	1.6	—	2.8
9	4-Fluorostyrene	—		92.1	94.3	1.2	—	4.5
10		0.1		84.1	94.6	1.3	—	4.1
11	1-Hexene	—		95.9	97.4	—	—	2.6
12		0.1		88.7	97.5	—	—	2.5
13	1-Dodecene	—		91.4	98.1	—	—	1.9
14		0.1		84.7	98.0	—	—	2.0
15	Styrene	—	Triethylsilane	93.1	84.8	1.3	10.0	3.9
16		0.1		86.4	85.1	1.2	10.3	3.4

Reaction conditions: alkene 40 mmol; silane 44 mmol; S poison: benzothiazole.
Catalyst: *trans*-$Pt(PPh_3)_2(C{\equiv}CSiPh_3)_2$ (**4b**) 0.05% based on styrene; 90°C, 5 h.

When other alkenes such as 1-hexene, 1-dodecene, 4-methoxystyrene 4-fluorostyrene, 2-methylstyrene, 3-methylstyrene and 4-methylstyrene were used as one of the substrates, high levels of conversion and selectivity were obtained when using **4b** as catalyst (Table 3). At the same time, **4b** did not lose its catalytic activity in the presence of trace amounts of poisonous sulfur. Also, when triethylsilane replaced triethoxysilane as hydrogen donor, the unsaturated adduct triethyl (styryl) silane was found.

Conclusion

In summary, a series of platinum acetylide complexes were synthesized. In comparison with Speier's catalyst, Karstedt's catalyst and **3a**, when the hydrosilylation reaction was undertaken using a series of platinum–acetylide–phosphine (**1b–8b**) as the catalysts, both higher catalytic activity and selectivity for the β-adduct were obtained. At the same time, the platinum–acetylide–phosphine complexes (**1b–8b**) did not lose their catalytic activities in the presence of small amount of poisonous sulfur. It can therefore also be assumed that alkyne ligands containing the silyl group played an important role in the hydrosilylation reaction. The platinum–acetylide–phosphine complexes (**1b–8b**) exhibited a strong ability to resist sulfur poisoning. Also, alkyne ligands containing a silyl group had a strong impact on the hydrosilylation reaction.

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