Synthesis of hexenyl aryl tellurides and the catalytic activity of their platinum(II) complexes as polysiloxane-supported catalysts in hydrosilylation of olefins

Ali Z. Al-Rubaie¹* and Zainab K. Al-Khazragie²
¹College of Pharmacy, Al-Ayen University, Nasiriya, Thi-Qar, Iraq
²Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq.
alrubaie49@yahoo.com

Abstract
5-hexenyl 1-naphthyl telluride (1) and 5-hexenyl (1,1’-binaphthyl-2-yl) telluride (2) were prepared from the reaction of 1-bromonaphthalene and 2-bromobinaphthalene with di(5-hexenyl) ditelluride in presence of lithium metal. Reaction of 1 and 2 with K₂PtCl₄ afforded the platinum(II) complexes 3 and 4, respectively in good yields. Silica-bound telluride-platinum complexes were directly synthesized from fumed silica, triethoxysilane and platinum complexes (i.e. 3 and 4). The catalytic activities of polysiloxane-supported platinum complexes were examined with 1-hexene, 1-decene and 1-dodecene at different temperature. It was found that these catalysts are efficient for hydrosilylation of olefins with triethoxysilane.

Keywords: Hexenyl aryl tellurides; Platinum (II) complexes; Hydrosilylation; Supported catalyst; Silica.

INTRODUCTION
Hydrosilylation of unsaturated C=C bonds is extensively studied in recent years.¹-³ A various platinum complexes containing phosphine, nitrogen or sulfur ligands have been synthesized and used as catalysts for hydrosilylation of unsaturated carbon-carbon bonds.⁴-⁶ Several platinum complexes containing selenium ligands and polysiloxane-supported selenium-platinum complexes exhibited a good catalytic activity toward hydrosilylation.⁷-⁹ On the other hand, many organotellurium compounds have been used as ligands to prepare palladium and platinum complexes that are stable at room temperature but they have not been used as catalysts for hydrogenation or hydrosilylation of olefins, as far as we aware. Thus, the present work describes the
synthesis of new tellurides, their platinum complexes and the silica-bound platinum-telluride complexes. Furthermore, the catalytic activity of the platinum complexes and their polysiloxane-supported catalysts will be tested with 1-hexene, 1-decene and 1-dodecene.

EXPERIMENTAL
Physical measurements

IR spectra were recorded as KBr discs in the range 4000-200 cm⁻¹ using a Pye-Unicam SP3-300s spectrophotometer. NMR spectra were obtained with a Varian VXR-200 spectrometer using TMS as an internal standard. Microanalysis of carbon, hydrogen and nitrogen were carried out by a Carlo Erba EA 1108-Elemental Analyzer instrument. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Tellurium analysis was carried out by use of a Shimadzu-AA30-32 atomic absorption spectrophotometer and as described previously. Platinum was determined by spectrophotometric methods according to a literature method. GLC determinations were carried out on a Hewlett Packard-5840A chromatograph equipped with a 6mX1/8 column of OV-17 on chromosorb w. Mass spectra were measured with a MAT 1125 Finnigan mass spectrometer; peaks shown relative to Te.

Synthesis

Air-sensitive reagents were manipulated in a pre-purified dry nitrogen atmosphere by using standard Schlenk technique. All solvents were dried and freshly distilled under nitrogen before use.

Di(5-hexenyl) ditelluride

A mixture of finely powder tellurium (3.60g; 28.2 mmol) and dry powdered potassium cyanide (1.84g; 28.2 mmol) in dry DMSO (25 ml) was heated at 100°C with stirring for 1 h when almost tellurium dissolved. To the resulting solution, diluted with DMSO (25 ml) and cooled to room temperature, was added a solution of 5-hexenyl bromide (4.60g; 28.2 mmol) dropwise during 30 min. After 2 h the pale-yellow solution was rapidly filtered from small amount of tellurium, poured into water (500 ml) and left for 12 h. A yellow precipitate of 5-hexenyltellurocyanate was obtained. This product was collected by filtration and dissolved in ethanol (25 ml) then a solution of sodium hydroxide (0.16g; 2.45 mmol) in 15 ml of dry ethanol was added to it. The resulting mixture was stirred for 30 min at 50°C under oxygen atmosphere. The solution was then refluxed for 1h, cooled to room temperature and filtered. The filtrate was acidified with 10% hydrochloric acid. A red viscous oil compound was formed. The oil was purified on a silica gel column with mixture of methanol and dichloromethane (1:4) as eluent to give a red oil of di(5-hexenyl) ditelluride in 37% yield.

Anal. Found: C, 34.01; H, 5.12; Te, 60.35. C₁₂H₂₂Te₂ Calc.: C, 34.19; H, 5.26; Te, 60.55%.

IR (cm⁻¹): 3080, 2925, 2850, 1640, 1460, 990, 900, 715.530, 482.

¹H NMR (CDCl₃) δ ppm: 1.25 (m, 4H), 1.75(m, 4H), 2.78(m, 4H), 3.21(t, 4H); 4.98(m, 4H), 5.69(m, 2H).

¹³C NMR(CDCl₃): 21.3, 30.4, 31.8, 32.9, 113.7, 138.7.

Mass spectrum: m/z 213(CH₂=CH(CH₂)₅Te⁺), 199(C₅H₅Te⁺), 186 (C₅H₄Te⁺), 158(C₂H₄Te⁺), 144(CH₂Te⁺), 130(Te⁺), 83, 69, 55, 42, 41.

Synthesis of 5-hexenyl 1-naphthyl telluride (1)

Di(5-hexenyl) ditelluride (2.11 g, 5 mmol) was dissolved in 100 mL of dry tetrahydrofuran (THF) and the solution was kept under an inert atmosphere of nitrogen. Small pieces of lithium (0.70g, 10 mmol) was added to this solution with stirring. The resulting solution was stirred at room temperature for 6-8 h until the solution became yellowish. The unreacted lithium was removed. To this solution, 1-bromonaphthalene
(2.07g; 10 mmol) was added dropwise with continuous stirring. The reaction mixture was stirred for 1 hour at room temperature, refluxed for 3 hours and then filtered. The filtrate was washed with water and the organic layer was separated and evaporated on a rotary evaporator to give yellow oil. The oil was purified on a silica gel column with petroleum ether (60-84°C) as eluent to give a yellow precipitate of compound 1 (m.p. 82-84°C).

**Anal. Found:** C, 56.53; H, 5.24; Te, 37.49. C_{16}H_{18}Te Calc.: C, 56.87; H, 5.36; Te, 37.76%.

**IR (cm⁻¹):** 3160, 3085, 2930, 2853, 1625, 1452, 995, 890, 710, 530, 452.

**1H NMR:** (CDCl₃) 1.31 (m, 2H); 1.63 (m, 2H); 2.78 (m, 2H); 3.01 (t, 2H); 4.98-5.12 (m, 2H); 5.75 (m, 1H); 7.31-7.39 (m, 4H); 7.47-7.88 (m, 3H).

**13C NMR:** (CDCl₃) 18.1, 26.4, 28.1, 28.3, 29.4, 30.2, 113.6, 125.0, 127.1, 128.6, 129.5, 130.2, 132.0, 134.6, 135.6, 139.6.

**Mass spectrum (selected data):** m/e: 314 (M-C₂H₂)+, 289 (M-C₄H₃)+, 213 (M-C₁₀H₇)+, 257 (C₈H₇Te+), 144 (CH₂Te+), 130, 127, 102, 55, 28.

**5-Hexenyl (1,1′-binaphthyl-2-yl) telluride (2).**

2-Bromo-1,1-binaphthyl (8.33g; 25 mmol), lithium (13 ml, 1.93M, 25 mmol) and di(5-hexenyl) ditelluride (6.32g; 15 mmol) in THF were treated by a procedure similar to that used for the preparation of 1, providing 2 (51% yield) as yellow precipitate, m.p. 111-113°C.

**Anal. Found:** C, 66.93; H, 5.18; Te, 27.62. C₂₆H₂₄Te Calc.: C, 67.29; H, 5.21; Te, 27.50%.

**IR (cm⁻¹):** 3170, 2075, 2935, 2850, 1573, 1448, 990, 885, 715, 535, 450.

**1H NMR:** (CDCl₃) 1.43 (m, 2H); 1.62 (m, 2H); 2.06 (m, 2H); 2.98 (t, 2H); 4.98 (m, 1H), 5.13 (m, 1H); 5.53 (m, 1H), 7.18-7.43 (m, 6H), 8.21-8.31 (m, 7H).

**13C NMR:** (CDCl₃) 20.8, 26.2, 27.9, 28.0, 29.7, 30.1, 113.7, 121.5, 125.0, 127.0, 128.0, 129.1, 132.2, 134.0, 135.3, 135.6, 139.6, 141.2, 145.5.

**Mass spectrum (selected data):** m/e: 414 (M-C₄H₄)+, 414 (M-C₄H₄)+, 256 (C₁₀H₆Te+), 253 (C₂₀H₁₃)+, 144 (CH₂Te+), 130, 127 (C₁₀H₇)+, 102 (C₈H₆)+, 55, 28.

**Dichloro(5-hexenyl 1-naphthyl telluride)Platinum(II) (3).**

A mixture of compound 1 (0.49g; 1.2 mmol) and K₂PtCl₄ (0.42g; 1.0mmol) in 25ml was stirred at 40°C for 24 hours under nitrogen atmosphere. A yellow precipitate was formed, collected by filtration. The product was washed with water, ether and dried in vacuo.

Complex 3 was obtained in 76% yield, m.p 132-134°C.

**Anal. Found:** C, 31.37; H, 2.96; Te, 20.71%. C₁₆H₁₈TePtCl₂ Calc.: C, 31.82; H, 3.00; Te, 21.13%.

**IR (cm⁻¹):** 3170, 3080, 2930, 2853, 1556, 1450, 992, 894, 715, 521, 445, 345, 314

**1H NMR:** (CDCl₃) 1.24-1.72 (m, 4H); 2.93-3.036 (m, 2H); 4.67-5.62 (m, 3H); 7.31-7.45 (m, 4H); 8.10-8.31 (m, 9H).

**13C NMR:** (CDCl₃) 17.65, 26.4, 28.1, 28.3, 29.4, 30.2, 113.6, 125.0, 127.1, 128.6, 129.5, 130.2, 132.0, 134.6, 131.6, 133.6.

**Dichloro(5-hexenyl (1,1′-binaphthyl-2-yl) telluride)Platinum(II) (4).**

A mixture of compound 2 (0.40g; 1.2 mmol) and K₂PtCl₄ (0.42g; 1.0mmol) in 25ml was stirred at 40°C for 24 hours under nitrogen atmosphere. A yellow precipitate was formed, collected by filtration. The product was washed with water, ether and dried in vacuo.

Complex 4 was obtained in 85% yield, m.p. 98-100°C.

**Anal. Found:** C, 42.27; H, 3.21; Te, 16.93%. C₂₆H₂₄TePtCl₂ Calc.: C, 42.78; H, 3.31; Te, 17.48%.
IR (cm⁻¹): 3175, 3076, 2925, 2850, 1558, 1445, 990, 890, 710, 520, 440, 345, 315.

¹H NMR(CDCl₃): 1.28-2.09(m, 6H); 2.87-2.96(m, 2H); 4.67-5.62(m, 3H); 7.30-7.42(m, 6H); 8.14-8.36(m, 7H).

¹³C NMR(CDCl₃): 17.9, 33.1, 33.2, 33.3, 114.9, 125.3, 125.7, 126.0, 126.4, 126.6, 126.7, 126.8, 126.8, 127.2, 127.4, 127.5, 127.6, 128.0, 128.3, 128.4, 132.1, 132.5, 134.8, 135.4.

Silica-bound dichloro(undecenyl 1-naphthyl telluride)platinum(II) (5).

Complex 3 (13.5mg; 0.02mmol) was allowed to react with triethoxysilane (3.4g; 20.8mmol) at 70 °C for 12 h under nitrogen atmosphere. Extra triethoxysilane was removed by distillation under reduced pressure to give 0.4g of brown-yellow oil. Toluene (10ml) and fumed silica (0.2g) were added to the resulting brown-yellow oil. The reaction mixture was stirred at 80 °C for 36 h under nitrogen atmosphere. The reaction mixture was cooled to room then distilled water added to the reaction mixture. The cooled mixture was stirred for 12 h. The cooled mixture was filtered, washed with acetone and dried in vacuo. A black precipitate was obtained. Anal. Found: Pt, 1.59; Te, 0.55 %.

Silica-bound dichloro(undecenyl 2-binaphthyl telluride)platinum(II) (6).

The same above procedure was used to obtain 5 as gray precipitate using complex 4 (16.0mg; 0.02 mmol) as substrate. Anal. Found: Pt 1.98; Te, 0.89 %.

Hydrosilylation of olefins

Hydrosilylation was carried out in round-bottomed flask equipped with a magnetic stirrer and reflux condenser. A drying system was attached to the upper of the condenser. Olefin and platinum complex were stirred at the reaction temperature (40, 60 and 80 °C) for 60 min before triethoxysilane was added. The structure and the yield of hydrosilylation products were determined by GLC by using a standard sample and a standard curve at regular intervals. Typical conditions were by using 10 mmol of HSi(OEt)₃, 10 mmol of olefin and 10⁻³ – 10⁻⁴ mmol of platinum.

RESULTS AND DISCUSSION

Reaction of 1-bromonaphthalene and 2-bromobinaphthalene with di(5-hexenyl) ditelluride, which in turn prepared from the reaction of hexenyl bromide with KTeCN followed by hydrolysis with NaOH, in presence of lithium metal gave tellurides 1 and 2 in fair yield, Scheme 1. Reaction of K₂PtCl₄ with 1 and 2 gave the platinum(II) complexes 3 and 4, respectively in good yield. The elemental analysis of compounds 3 and 4 indicated that the tellurides (1 and 2) coordinated with platinum(II) in 1:1 molar ratio. The IR spectra of these new complexes show a decrease in the C=C stretching frequency of about 85 cm⁻¹; for example, vC=C drops from 1640 cm⁻¹ for the free ligand to 1555 cm⁻¹ in complex 3, see Experimental section. Furthermore, two typical Pt-Cl peaks are present in the spectra of compounds 3 and 4 at around 345 and 315 cm⁻¹. This indicates the cis-configuration of these complexes⁶⁻⁹. In the IR spectra of all complexes, the v(Te-C) consist of two bands with a red shift of ~10 cm⁻¹ in compares with the free ligands. The chemical shifts of vinyl protons at ~ 5.80, 5.01 and 4.92 ppm changed to a broad multiplet at 4.83-5.22 ppm and the Te-CH₂ protons also deshielded by ~ 0.4 ppm. This indicates that each telluride is acting as unsymmetrical bidentate ligand which coordinates with platinum through Te atom and C=C bond, Scheme 1.

The polysiloxane-supported telluride platinum complexes were prepared from the reaction of the telluride-platinum complexes (i.e 3 and 4) with triethoxysilane and silica, Scheme 1.

The catalytic behavior of complex 3 was examined by using 1-hexene, 1-decene and 1-dodecene as substrates. The substrates were hydrosilylated with HSi(OEt)₃ by stirring the olefin and platinum complex for 60 min followed by addition of triethoxysilane to give hexyltrioethoxysilane, decyltrioethoxysilane and...
dodecyltriethoxysilane in 88, 85 and 78% respectively. The catalytic activity of complex 4 was also examined with 1-hexene, 1-decene and 1-dodecene by the same procedure and gave the saturated products in 83, 80 and 73% respectively. As it is known\(^\text{15}\) that hydrosilylation of 1-decene with triethoxysilane gave decyltriethoxysilane in 40% yield when H\(_2\)PtCl\(_6\) was used as catalyst.

The catalytic activity of complex 3 was examined at 40, 60 and 80°C using 1-decene and triethoxysilane as a model reaction. The experimental results indicated that no remarkable induction period was observed and the reaction rate became faster. In the range 40 to 80°C, the catalytic reaction finished within 50 min, Fig. 1.

The hydrosilylation of 1-decene with triethoxysilane was also examined by using the supported catalysts 5 and 6. It was observed that the reaction rate increased with the increase of temperature and the final yields of saturated products were similar within the same temperature range. In general, the yield of decyltriethoxysilane decreased with the increasing runs. For complex 3, the yields of decyltriethoxysilane from first run to 50\(^\text{th}\) run were decreased from 87% to 39%. The supported catalysts 5 and 6 had better reusable properties than complex 3. The yields of decyltriethoxysilane from the first run to 50th run were from ~88% to ~74%, Fig. 2.

In conclusion a new organotellurium compounds were prepared together with their platinum(II) complexes. These new tellurium-platinum complexes are efficient for the hydrosilylation of olefins. The supported silica-bound telluride-platinum complexes were found to be efficient in hydrosilylation of olefins and had better reusable properties than telluride-platinum complexes.

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\text{Scheme 1. Preparative methods for compounds 1 – 6.}
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Fig. 1. Plot of the yield of decyltriethoxysilane against time with 3 (---) and 6 (——) as catalysts. ◦ at 40°C. □ at 60°C. ■ at 80°C.

Figure 2. Plot of the yield of decyltriethoxysilane against number of runs at 80°C for 3, 5 and 6.