THERMAL DECOMPOSITION OF VINYL- AND ALLYLSILANE PLATINUM(II) COMPLEXES AND PLATINUM(II) CATALYSED SYNTHESIS OF \((E),(E)-1,4\)-DIPHENYL-1,3-BUTADIENE

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**ABSTRACT.** Thermal stabilities of Pt(II) complexes: \(K\left[PtCl_3(CH_2=CHSiMe_3)\right]\), \(K\left[PtCl_3(CH_2=CHCH_2SiMe_3)\right]\), \(K\left[\text{acac}PtCl(CH_2=CHSiMe_3)\right]\) and \([\text{PtCl}(CH_2=CHCH_2SiMe_3)]_2\), were examined. All complexes were found to be stable at room temperature but they decomposed without melting above about 90 °C. The allylsilane complex decomposed above about 125 °C. All complexes liberated chlorotrimethylsilane on decomposition, showing the facile cleavage of the C–Si bond by nucleophilic attack on the silicon by the chloride ion. \((E),(E)-1,4\)-diphenyl-1,3-butadiene was stereoselectively synthesised in good yield from \((E)\)-\(\beta\)-styrylsilane in the presence of Zeise’s salt.

**KEY WORDS:** Thermal analysis, Vinyl- and allylsilane platinum(II) \(\pi\)-complexes, Platinum(II) catalysed synthesis, \((E),(E)-1,4\)-diphenyl-1,3-butadiene

**INTRODUCTION**

Reports describing the kinetics and mechanisms of hydrolyses of uncoordinated vinyl- and allyltrimethylsilanes, catalysed by mercury(II) and palladium(II) chlorides, have appeared in the literature [1, 2]. The products of these reactions are mainly alkenes and hexamethyldisiloxane. Fitch and co-workers have successfully prepared \(\pi\)-coordinated vinyl- and allylsilane complexes of platinum(II) [3, 4], \((1a, 1b, 2\text{ and } 3)\). These complexes are stable at room temperature in a desiccator but hydrolysed easily to give mainly hexamethyldisiloxane, propene and acetone as organic products [5]. The vinyl- and allylsilane platinum(II) complexes \((1a, 1b, 2\text{ and } 3)\) generally decompose and hydrolyse by cleavage of the polar \(C^\beta—Si^{\delta+}\) bond through nucleophilic substitution on the silicon atom [3, 5]. In this paper we report on the investigation of thermal stabilities of vinyl- and allylsilane platinum(II) complexes \((1a, 1b, 2\text{ and } 3)\), and the synthesis of \((E),(E)-1,4\)-diphenyl-1,3-butadiene \(4\) from \(\beta\)-styrylsilane. The paper is part of a systematic investigation of properties of vinyl- and allylsilane platinum(II) complexes and their use in stereoselective synthetic organic chemistry.

\[ \text{K}^{+}\left[PtCl_3(CH_2=CHSiMe_3)\right] \]

\[ \text{K}^{+}\left[PtCl_3(CH_2=CHCH_2SiMe_3)\right] \]

\[ K\left[\text{acac}PtCl(CH_2=CHSiMe_3)\right] \]

\[ [\text{PtCl}(CH_2=CHCH_2SiMe_3)]_2 \]

\[ \text{Ph}—\text{C}—\text{C}—\text{Ph} \]

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EXPERIMENTAL

Reactions were performed under nitrogen by use of Schlenk techniques. Solvents were dried by standard methods and distilled before use. IR spectra were recorded on a Beckam IR-10 spectrophotometer. NMR spectra were obtained on a Perkin-Elmer P-12A spectrometer. Commercial reagents were of AR grade, but β-styryltrimethylsilane was prepared in our laboratory by a Grignard-type reaction from β-bromostyrene and chlorotrimethylsilane. Samples of complexes 1a-3 were prepared by literature methods [3, 4].

Thermogravimetric analyses. Analyses were performed on a Cahn, “little gem” system with a model RM-2 electrobalance, which was calibrated with copper sulfate pentahydrate. Samples were gradually heated to 275 °C and the weight losses recorded at 5 °C intervals.

Pyrolyses. In a typical experiment, samples of about 250 mg of complexes were placed in a Schlenk tube and slowly heated to 210 °C in a silicone oil bath. The volatile products were collected in a trap at −79 °C and transferred into an evacuated IR gas cell. The residues were extracted with acetone and the soluble species identified by means of IR and 1H NMR spectroscopy.

Preparation of (E)-β-styryltrimethylsilane. To a dry flask containing magnesium (3.6 g, 0.015 mol), a solution of β-bromostyrene (2.5 g, 0.014 mol) in absolute ether was added with stirring. Initially 10 mL of the solution was added and the remainder after 20 min. The mixture was cooled in an ice-bath and chlorotrimethylsilane (1.48 g, 0.014 mol) in 20 mL dry ether was added to the stirred solution. The mixture was stirred at room temperature for 20 min and hydrolysed by pouring it into conical flask containing 25 mL ice-water and 20 mL 10 % H2SO4. The ether layer was washed with saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. After removal of solvent, the residue was distilled under reduced pressure (86 °C, 20 mmHg) to yield (E)-β-styryltrimethylsilane (65 %).

Synthesis of (E),(E)-1,4-diphenyl-1,3-butadiene. β-Styryltrimethysilane (2.0 mL, 10.5 mmol) was added to a stirred solution of Zeise’s salt, K[PtCl3(CH2=CH2)] [3] (1.1 g, 3.1 mmol) in dry acetone (10 mL). Ethylene was evolved briskly and after 15 min the solution turned dark. It was stirred at room temperature for 6 h. and filtered through celite. Solvent was removed from the filtrate (GC analysis indicated the presence of chlorotrimethylsilane) and the residue was crystallised from pentane to give tan crystals of (E),(E)-1,4-diphenyl-1,3-butadiene 4 in 65 % yield and m.p. 150-151 °C. The IR and 1H NMR spectra of the product were in agreement with those in the literature [6].

RESULTS AND DISCUSSION

The platinum(II) complexes (1a, 1b, 2, 3) used in this study were prepared previously and their hydrolytic stabilities investigated [4, 5]. Their thermal stability has not been investigated.

Pyrolytic cleavages. Volatile products of the thermal treatment of the complexes were analysed by GC, IR and 1H NMR. Chlorotrimethylsilane was observed to be the main product as shown by bands at 2960, 1255, 1065 and 840 cm⁻¹, observed in an authentic sample. The spectrum also showed bands at 3080, 3032, 1590, 940 and 910 cm⁻¹, indicating the presence of olefinic products. The 1H NMR spectrum in CDCl3 showed two singlets at δ 0.40 and 0.02 assigned to the methyl groups of chlorotrimethylsilane and hexamethyldisiloxane, respectively. Weak multiplets at δ 5.23 and 4.35 were assigned to olefinic protons and a singlet at δ 2.12 was attributed to acetone. Olefinic volatile products and acetone were detected in small quantities and therefore could not be quantitatively estimated.
The presence of small amounts of hexamethyldisiloxane and acetone are attributed to the hydrolysis of chlorotrimethylsilane and allylsilanes by water, which was detected in the IR spectra of the starting complexes. The brown residues from the pyrolyses were extracted with acetone and the solution filtered. The soluble fractions showed IR spectra like those of CH$_2$=CHPtCl and CH$_2$=CHCH$_2$PtCl described earlier [5]. The formation of these platinum compounds is proposed in Scheme 1.

Scheme 1. Proposed mechanisms for the thermal decomposition of vinyl- and allylsilane platinum(II) complexes.

**Thermogravimetric analysis (TGA).** The TGA curves in Figure 1 show that, except for complex 1b, complexes 1a, 2 and 3, initially lose about 3–4% of water which may be water of hydration. The IR spectra of these complexes showed weak broad bands at 3600 cm$^{-1}$ due to water although the complexes were dried in vacuo over phosphorus pentoxide.

Complex 1a showed a weight loss of about 23% from about 90 to 140 °C, attributed to Me$_3$SiCl. Complex 2 started decomposition from 90 to 135 °C and showed a weight loss of about 40%, attributed to loss of chlorotrimethylsilane and acetylacetonato (acac) ligand. Complex 3 decomposed from about 100 °C to 165 °C and had a weight loss of about 39% corresponding to the elimination of chlorotrimethylsilane and the allyl group. In contrast, complex 1b decomposed gradually at higher temperature, from about 125 to 190 °C showing a weight loss of 24% corresponding to the loss of chlorotrimethylsilane. The calculated weight losses of volatile products are in good agreement with the expected theoretical loss based on dry weights. The results indicate that chlorotrimethylsilane is thermally eliminated from all the complexes, thus showing that the complexes undergo a facile cleavage of the carbon-silicon bond. The pyrolyses described above also indicated that chlorotrimethylsilane was the major volatile product. The high residual weights for 1a and 1b are consistent with the presence of alkenylplatinum chlorides, as shown in the separate pyrolyses, as well as KCl. The increasing order of thermal stabilities of the complexes is observed to be from 2, 3, 1a and 1b.
The formation of chlorotrimethylsilane, vinylplatinum chloride and allylplatinum chloride are suggested in Scheme 1. The products are formed by the nucleophilic attack of the chloride ion on silicon and the subsequent cleavage of the C–Si bond.

Figure 1. Thermogravimetric analyses of complexes 1a, 1b, 2 and 3.

Synthesis of (E),(E)-1,4-Diphenyl-1,3-Butadiene. The synthesis of (E),(E)-1,4-diphenyl-1,3-butadiene 4 proceeded smoothly and gave a yield of 65 %. In contrast to trimethylvinylsilane and allyltrimethylsilane, the ligand (E)-β-styryltrimethylsilane did not form a stable platinum(II) π-complex when treated with Zeise’s salt, using the standard procedure [4]. During the reaction a brisk evolution of ethylene was observed and the mixture turned grey. Work-up gave 4 and chlorotrimethylsilane. The evolution of ethylene during the reaction showed that ethylene gas was displaced by the styryltrimethylsilane to form an unstable (E)-β-styryltrimethylsilane π-platinum(II) complex that decomposed to give 4. The identity of 4 was established by its m.p. (150-152 °C), 1H NMR and IR spectra, which were identical to those of a sample prepared by use of a Pd based catalyst [6]. The reaction is stereoselective and gave a good yield of 4. It has potential for the syntheses of other aryl analogues.

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REFERENCES