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HYDROLYSIS OF ALLYLSILANES COORDINATED TO PLATINUM(II)

JOHN W. FITCH, MICHAEL BROWN, NANCY H. HALL, PAUL P. MEBE, KEVIN A. OWENS, and MICHAEL R. ROESCH

Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666 (U.S.A.)

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Summary

Allylsilane complexes of formula, $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$, $[(acac)\text{-}PtCl(CH_2{=}CHCH_2SiMe_3)]$ and *trans*-$[PtCl_2(py)CH_2{=}CHCH_2SiMe_3)]$ where py = a pyridine base, have been prepared, isolated and hydrolyzed. In the cases studied the major product of the hydrolysis is an allyl-platinum(II) complex rather than propene. Propene complexes can be formed, however, if the hydrolysis is conducted at sufficiently low pH.

Introduction

Allylsilanes are known to undergo both nucleophilic and electrophilic cleavage of the silicon–carbon bond [1,2]. Recent evidence indicates that such cleavage reactions are facilitated upon coordination of the allylsilane to certain transition metal ions, and the products of these cleavages depend on the metal involved as well as on reaction conditions.

For example, allyltrimethylsilane reacts with palladium(II) chloride in wet solvents to form dimeric η^3-allylpalladium(II) chloride along with propene and hexamethyldisiloxane [3]. The propene is thought to originate form a secondary reaction involving electrophilic cleavage of the allylsilane by the hydrochloric acid which is generated as the primary reaction proceeds to form the π-allyl complex. Evidence for this conclusion is derived from the observation that propene is not generated when palladium(II) acetate replaces the chloride in this reaction [3].

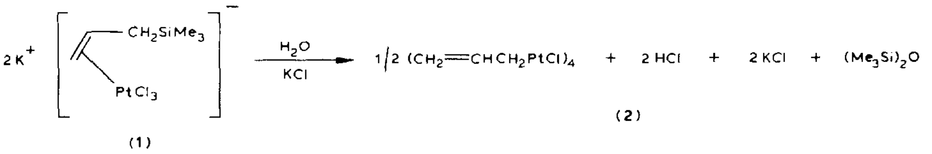
Potassium tetrachloroplatinate(II) is also known to cleave allyltrimethylsilane to tetrameric allylplatinum(II) chloride in good yield [4]. This reaction is conducted in four percent hydrochloric acid in the presence of excess allyltrimethylsilane, and only traces of potassium (η^2-propene)trichloroplatinate(II) are observed. This result contrasts with a recent observation that allytrimethylsilane reacts stoichiometrically with water in deuterochloroform in the presence of Zeise's dimer to yield only propene and hexamethyldisiloxane [5].

Clearly, factors responsible for the formation of allyl complexes in the one case and propene in the other need to be defined. With this goal in mind we have prepared, isolated and then hydrolyzed several η^2-allytrimethylsilaneplatinum(II) complexes and report our results at this time.

Results and discussion

Hydrolysis of allyltrimethylsilane derivatives of Zeise's salt and dimer

Potassium (η^2-allyltrimethylsilane)trichloroplatinate(II) (**1**) is hydrolyzed in aqueous potassium chloride to form **2** (identical to an authentic sample [6]) in high yield. Only very small quantities of the propene complex, $K[PtCl_3(CH_2{=}CHCH_3)]$, are observed in the acidic filtrate remaining after isolation of **2** (maximum concentration of HCl estimated to be less than 0.05 *M*). Interestingly, the yield of **2** (70 to 90%) is not significantly affected when the concentration of potassium chloride is varied from 0.5 *M* to saturated.



Compound **1** also forms **2** in good yield when hydrolyzed in wet acetone; however, it yields only the propene complex when hydrolyzed in acetone containing six percent 6 *N* hydrochloric acid (approximately 0.4 *M* in HCl). These results suggest that the pH at which **1** is hydrolyzed affects the yield distribution between **2** and the propene complex.

When the hydrolysis is conducted in pure water a yellow insoluble compound **2a** which is similar to **2** is formed (see Fig. 1 for the IR spectra of **2** and **2a**). Compound **2a** has an elemental composition identical to that of **2**. It is formulated as an allyl complex since it reacts with triphenylphosphine, as does **2**, to form the known compound [7], $[(\eta^3\text{-}C_3H_5)PtCl(PPh_3)]$, in good yield and with sodium cyclopentadienide to form $[(\eta^3\text{-}C_3H_5)Pt(\eta^5\text{-}C_5H_5)]$ [7] in modest yield. However, in the reaction with triphenylphosphine, **2a** differs from **2** in being initially soluble in the reaction mixture of tetrahydrofuran and the phosphine. This difference in reactivity coupled with the considerable differences in the IR spectra of the two compounds, especially in the 1350–1500 cm^{-1} and 3000 cm^{-1} regions, indicates that **2a** is indeed different from **2**, but its elemental composition and the reactions with the two derivatizing reagents indicate that the difference is not great. Consequently, **2a** is formulated as $[C_3H_5PtCl]_x$, an isomer or oligomer of **2**.

The reason for the formation of **2a** rather than **2** in the absence of potassium chloride is not clear at this time; however, it is clear that allylplatinum(II) species, not propene complexes, are the primary hydrolysis products of **1** in pure water or aqueous potassium chloride solutions. Similar results are obtained for the dimeric analogue of **1**, $[PtCl_2(CH_2{=}CHCH_2SiMe_3)]_2$.

The contrast between these results and those observed earlier [5] which indicate that the hydrolysis of allyltrimethylsilane in the presence of Zeise's dimer yields only propene might be explained in terms of solvent effects. The earlier work was conducted in $CDCl_3$ in the presence of a stoichiometric amount of water and yielded

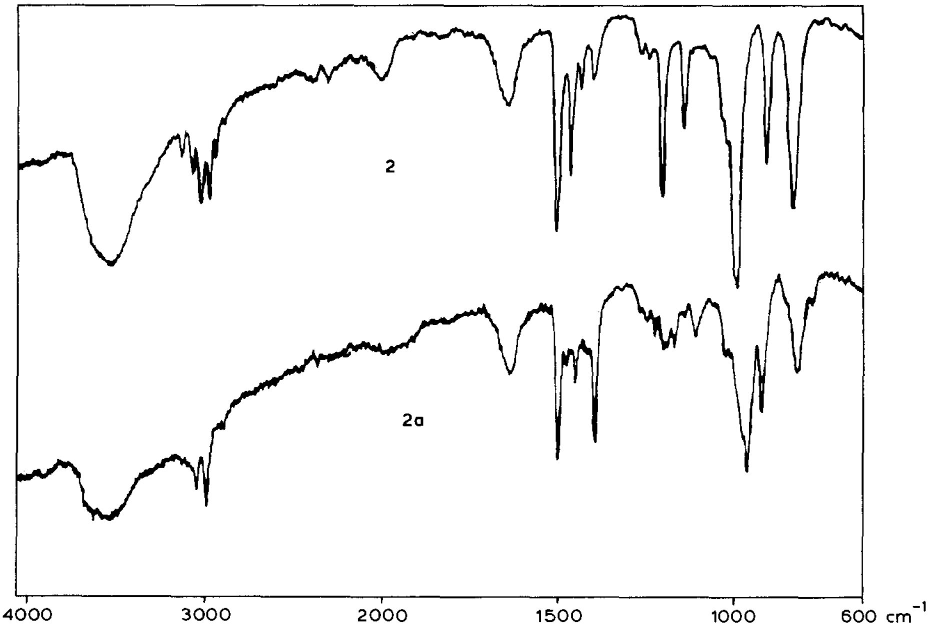
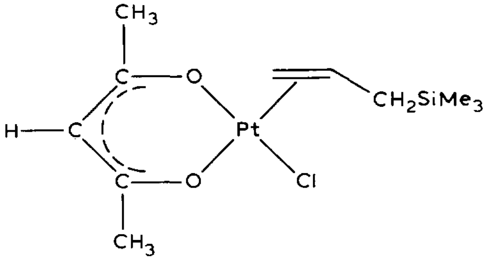


Fig. 1. IR spectra of $(CH_2{=}CHCH_2PtCl)_4$ (**2**) and $(C_3H_5PtCl)_x$ (**2a**) (KBr pellets).

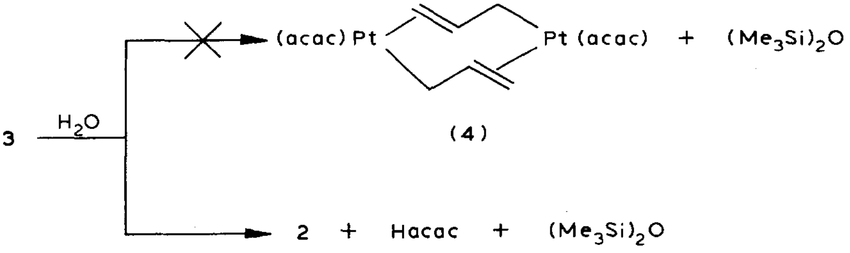
hydrogen chloride as an intermediate according to the proposed mechanism [5]. This strong acid, which is not ionized in the non-basic solvent, is known to cleave allylsilanes to propene [1]. In deuterochloroform this reaction must be dominant.

In order to demonstrate that allylplatinum(II) complexes are generally formed from the hydrolysis of platimum(II) coordinated allyltrimethylsilane in basic solvents, two more examples were investigated. Compound **3** does not yield the expected



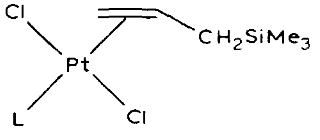
(3)

allyl-bridged dimer [7] **4**, in which the chelating acetylacetonato ligand is retained,



but rather forms **2** in excellent yield when hydrolyzed in wet acetone. It is interesting to note that the very weak acid acetylacetone is released in this hydrolysis and propene is not formed.

Further indication of the importance of pH control in the hydrolysis of coordinated allylsilanes is obtained from hydrolysis of complexes **5a** and **5b**. When **5a** or **5b** is hydrolyzed in wet acetone containing 1,8-bis(dimethylamino)naphthalene as a proton acceptor (to prevent possible protonation and dissociation of the pyridine base ligand [5]), the allyl complexes, $[(C_3H_5)PtCl(C_5H_5N)]$ or $[(C_3H_5)PtCl(C_9H_7N)]$, are obtained in 62 and 58 percent yield respectively. These complexes are identical to those obtained through reaction of **2** with the pyridine bases [7].



(5a L = pyridine ;
5b L = isoquinoline)

In summary, our results indicate that cleavage of the silicon–carbon bond in platinum(II)-coordinated allyltrimethylsilane yields allylplatinum(II) complexes when conducted in basic solvents such as water or acetone. However, in the presence of added acid the cleavage reaction can yield propene complexes. These results parallel those reported earlier for the interaction of allyltrimethylsilane with palladium(II) salts [3].

Experimental

Reactions were conducted in an atmosphere of pre-purified nitrogen or argon. IR spectra were determined utilizing KBr wafers on a Beckman IR-10 spectrometer. Carbon and hydrogen were determined locally on a Coleman model 33 analyzer or by Galbraith Laboratories, Knoxville, Tennessee. Allyltrimethylsilane was obtained from Petrarch Systems, Levittown, Pennsylvania. Samples of $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ [4], $[PtCl_2(CH_2{=}CHCH_2SiMe_3)]_2$ [4], $[(CH_2{=}CHCH_2PtCl)_4]$ [6], *trans*-$[(CH_2{=}CH_2)PtCl_2(L)]$ [8], and $[(C_3H_5)PtCl(L)]$ [7] (L = pyridine or isoquinoline) were prepared by the literature methods and gave satisfactory carbon, hydrogen and spectral analyses. Tetrahydrofuran and pentane were distilled from calcium hydride prior to use.

Hydrolysis of $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$

In presence of KCl. In a typical reaction $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ (0.60 g, 1.3 mmol) was added to 25 ml of KCl solution, and the mixture was stirred for 24 h. The insoluble yellow reaction product which was isolated by filtration from the acidic reaction mixture was washed successively with water and acetone and then dried in vacuo over P_2O_5. Small amounts of $K[PtCl_3(CH_2{=}CHCH_3)]$ are detected by IR in the residue resulting from evaporation of the combined washings. Yield of

$(CH_2{=}CHCH_2PtCl)_4$ (IR identical to known sample) is 0.28 g (79%). Decomp.pt. 159–170°C. Anal. Found: C, 13.34; H, 1.86. $C_{12}H_{20}Cl_4Pt_4$ calcd.: C, 13.25; H, 1.85%. Although isolated yields of $(CH_2{=}CHCH_2PtCl)_4$ varied somewhat from run to run (70–90%) similar results were observed in 0.5 *M* and saturated KCl solutions.

In pure water. In a manner identical to that described above $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ (0.60 g, 1.3 mmol) is hydrolyzed in pure water (25 ml) to yield, after isolation and drying, 0.35 g of yellow insoluble product (decomp. pt. 150–156°C; 98% yield calcd. as $(CH_2{=}CHCH_2PtCl)_x$). Anal. Found: C, 13.23; H, 1.82; Cl, 12.77. $(C_3H_5ClPt)_x$ calcd.: C, 13.25; H, 1.85; Cl, 13.07%.

Hydrolysis of $[PtCl_2(CH_2{=}CHCH_2SiMe_3)]_2$ in aqueous KCl and pure water

$[PtCl_2(CH_2{=}CHCH_2SiMe_3)]_2$ (0.60 g, 0.79 mmol) was stirred with KCl solutions (25 ml of 2 *M* or saturated) for 24 h. The yellow products, identified as $(CH_2{=}CHCH_2PtCl)_4$ by IR were isolated from the acidic solutions as described before in yields of 0.38 g (88%) and 0.40 g (93%) respectively. The reaction was repeated using pure water and $(CH_2{=}CHCH_2PtCl)_x$, identical to that obtained above, was obtained in 88% yield.

Reaction of $(CH_2{=}CHCH_2PtCl)_4$ or $(CH_2{=}CHCH_2PtCl)_x$ with triphenylphosphine

In a typical reaction $(CH_2{=}CHCH_2PtCl)_4$ (0.50 g, 0.46 mmol) was mixed with PPh_3 (0.5 g, 1.8 mmol) in tetrahydrofuran (5 ml). The yellow suspension slowly turned white as it was stirred for 24 h after which the solvent was removed in vacuo. The white crystalline triphenylphosphine(allyl)chloroplatinum(II) [7] was washed several times with 10 ml portions of pentane and dried in vacuo. (Yield 0.90 g, 91%; m.p. 186°C, lit [7] m.p. 182–188°C) Anal. Found: C, 47.16; H, 3.56. $C_{21}H_{20}ClPPt$ calcd.: C, 47.25; H, 3.80%. In an entirely analogous reaction $(CH_2{=}CHCH_2PtCl)_x$ yields 0.94 g (95%) of triphenylphosphine(allyl)chloroplatinum(II) (m.p. 186°C) Anal. Found: C, 47.01; H, 3.81%.

Reaction of $(CH_2{=}CHCH_2PtCl)_4$ or $(CH_2{=}CHCH_2PtCl)_x$ with sodium cyclopentadienide

In a typical reaction $(CH_2{=}CHCH_2PtCl)_4$ (0.30 g, 0.28 mmol) was suspended in tetrahydrofuran (5 ml), and sodium cyclopentadienide (1.1 mmol) was added at −78°C. After the reaction was stirred for one hour as it warmed to room temperature, the solvent was removed in vacuo. The golden brown residue was washed with methanol (5 ml) and then taken up in pentane (30 ml). Crude cyclopentadienyl(allyl)platinum(II) (0.19 g) was obtained on removal of solvent in vacuo. A pure product was obtained upon sublimation at 0.1 Torr and 40°C. (Yield 0.05 g (15%) m.p. 62°C, lit [7] m.p. 63–64°C) Anal. Found: C, 31.93; H, 3.10. $C_8H_{10}Pt$ calcd.: C, 31.90; H, 3.35%. In an entirely analogous procedure $(CH_2{=}CHCH_2PtCl)_x$ gives an identical product in the same yield. Anal. Found: C, 31.87: H, 3.11%.

Hydrolysis of $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ in wet acetone

$K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ (1.52 g, 3.3 mmol) was dissolved in wet acetone (15 ml containing 2 ml H_2O) and stirred for 24 h. The product, $(CH_2{=}CHCH_2PtCl)_4$, was isolated by filtration. Yield 70%. IR identical to authentic sample. Similar results are obtained with $[PtCl_2(CH_2{=}CHCH_2SiMe_3)]_2$.

Reaction of $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ with 0.4 M HCl in acetone

Five drops of 6 *N* HCl were added to a solution of $K[PtCl_3(CH_2{=}CHCH_2SiMe_3)]$ (0.84 g) in acetone (4.0 ml). A precipitate of KCl formed immediately, and the reaction was allowed to stand for 24 h whereupon a sixth drop of HCl was added to assure completeness of precipitation. After 12 additional hours the precipitate was isolated by centrifugation and washed with acetone (UV VIS spectrum shows K_2PtCl_4 is also present). The yellow acetone solution was then evaporated in vacuo to yield a yellow oil which was crystallized when ether was added. Anal. Found: C, 9.36; H, 1.76. $C_3H_6Cl_3KPt$ calcd.: C, 9.42; H, 1.58%.

Preparation of $[PtCl(acac)(CH_2{=}CHCH_2SiMe_3)]$

Allyltrimethylsilane (3.0 ml, 19 mmol) was added to a stirred solution of $[PtCl(acac)(CH_2{=}CH_2)]$ [9] (1.60 g, 4.47 mmol) in benzene (50 ml). Ethylene gas was evolved from the stirred solution, and after three hours the reaction mixture was evaporated to dryness in vacuo to give a yellow product which was washed with hexane and vacuum dried. The bright yellow product (1.88 g, 95% yield) melts at 112–113°C. Anal. Found: C, 29.60; H, 4.73. $C_{11}H_{21}ClO_2PtSi$ calcd.: C, 29.75; H, 4.73%.

Hydrolysis of $[PtCl(acac)(CH_2{=}CHCH_2SiMe_3)]$ in wet acetone

$[PtCl(acac)(CH_2{=}CHCH_2SiMe_3)]$ (0.90 g, 2.0 mmol) dissolved in wet acetone (30 ml containing 0.5 ml H_2O) was allowed to stand in the dark for one week. At the end of this time $(CH_2{=}CHCH_2PtCl)_4$ was isolated in 92% yield by filtration. Anal. Found: C, 13.46; H, 1.90. $C_{12}H_{20}Cl_4Pt_4$ calcd.: C, 13.26; H, 1.84%. IR spectrum is identical to authentic sample. The pH of the solution had fallen to about 5–6 during the course of the reaction.

Preparation of trans-$[PtCl_2(L)(CH_2{=}CHCH_2SiMe_3)]$ (L = pyridine or isoquinoline)

Allyltrimethylsilane (3 ml) was added to a solution of *trans*-$[PtCl_2(L)(CH_2{=}CH_2)]$ (1.5 g) dissolved in acetone (10 ml). After the solution had been stirred for 30 min and ethylene evolution stopped, the solvent and excess ligand were removed in vacuo. The yellow product which was formed in quantitative yield was washed with pentane and vacuum dried. M.p. 108°C (L = pyridine); 96–98°C (L = isoquinoline). Anal. (L = pyridine) Found: C, 29.16; H, 4.11. $C_{11}H_{19}Cl_2NPtSi$ calcd.: C, 28.88; H, 4.20%. (L = isoquinoline) Found: C, 35.28; H, 4.17. $C_{15}H_{21}Cl_2NPtSi$ calcd.: C, 35.36; H, 4.12%.

Hydrolysis of trans-$[PtCl_2(L)(CH_2{=}CHCH_2SiMe_3)]$ (L = pyridine or isoquinoline)

The platinum complex (1.5 g) was stirred with a molar equivalent of 1,8-bis(dimethylamino)naphthalene in wet acetone (15 ml acetone and 2 ml water) for 24 h. The yellow precipitate was obtained by filtration, washed with water, cold acetone and pentane, and finally dried in vacuo. For L = pyridine, m.p. 155°C (Yield 62%). Anal. Found: C, 27.12; H, 2.79. $C_8H_{10}ClNPt$ calcd.: C, 27.38; H, 2.85%. For L = isoquinoline; m.p. 132°C, lit. [7] m.p. 135–139°C (Yield 58%). Anal. Found: C, 36.05; H, 2.90. $C_{12}H_{12}ClNPt$ calcd.: C, 35.95; H, 3.00%.

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