

Preliminary communication

THE COMPOSITION OF SPEIER'S CATALYST

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Summary

It is proposed that the very important and useful "Speier catalyst" contains the complex $H[(C_3H_5)_2PtCl_3]$ in a solution of isopropyl alcohol. It is this platinum complex which is the active catalyst ingredient in hydrosilylation reactions. When solvent was removed from an "aged" solution of chloroplatinic acid in isopropyl alcohol, the Zeise type dimer, $(C_3H_5)_2Pt_2Cl_4$, was deposited as an orange solid. This dimer underwent solvolysis and dissociated into a monomeric species when it dissolved in isopropyl alcohol. Spectroscopic methods involving ^{195}Pt NMR, 1H NMR (360 MHz), far infrared, IR and ESCA were employed in reaching these conclusions.

A solution of chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) dissolved in isopropyl alcohol (1 g/20 ml) is referred to as "Speier's" catalyst [1]. The reagent is widely used both in industrial and academic laboratories to effect the addition of a silanic hydride moiety ($\equiv SiH$) to a double or triple bond in an organic molecule (hydrosilylation). One of the many remarkable properties of this catalyst is that it can cause the rapid migration of double bonds in olefins to yield an equilibrium distribution of isomers [2]. As a consequence, hydrosilylation of 2-pentene with trichlorosilane and Speier catalyst formed only n-pentylchlorosilane in nearly quantitative yield [1].

Although a schematic mechanism for hydrosilylation has been proposed [3] and generally accepted as a working hypothesis, little is known about the composition of the catalyst itself. Several years ago, it was claimed [4,5] that the Speier catalyst contained chloroplatinic ($H_2Pt^{IV}Cl_6$), chloroplatinous acid ($H_2Pt^{II}Cl_4$) and also platinum metal itself resulting from a reduction of the various platinum species by the alcohol.

We wish to report that recent experiments from our Laboratory indicate that the Speier catalyst contains the complex, $H[(C_3H_5)_2PtCl_3]$, as the exclusive platinum species at least within the detection limits of the spectroscopic methods employed in this investigation (vide infra).

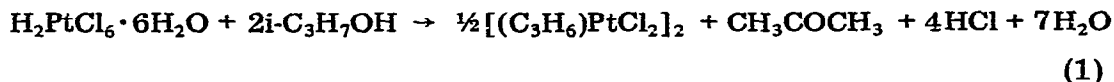
Chloroplatinic acid hexahydrate dissolved in isopropyl alcohol forms a reddish

solution [6]. The platinum(IV) is rapidly reduced at least in part [4,5] to platinum(II) by the isopropyl alcohol, affording acetone [4,5] as the oxidation product, and the red solution becomes gradually reddish-yellow. The rate of this redox reaction has been reported to be light sensitive [5].

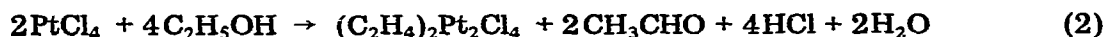
When a batch of two-week-old catalyst solution* was evaporated in vacuo below room temperature (to minimize any chemical changes), an orange solid remained. This solid gave an ESCA spectrum with a clean single peak for Pt ($4f_{7/2}$) centered at 72.7 eV binding energy, indicating that platinum(IV) had been reduced to platinum(II) to the extent of at least 99% [7]. This is exactly the same chemical shift for Pt ($4f_{7/2}$) reported [8] for the propyleneplatinum dimer, $(C_3H_6)_2Pt_2Cl_4$. An elemental analysis was carried out on the orange solid residue. Anal. Found: C, 11.90; H, 2.12; Cl, 23.30; Pt, 63.05; mol. wt. 605. $(C_3H_6)_2Pt_2Cl_4$ calcd.: C, 11.70; H, 1.96; Cl, 23.02; Pt, 63.33%; mol. wt. 616.

Mid- and far-infrared spectra of the orange solid residue in Nujol mull (Digilab FTS-20, resolution 4 cm^{-1}) matched those of an authentic sample of $(C_3H_6)_2Pt_2Cl_4$ [9,13]. Also the ^{195}Pt NMR spectrum of the solid in $CDCl_3$ (FT-80 NMR spectrometer, 2453 ppm upfield to Na_2PtCl_6 , computer locking) was within experimental error [10] to the authentic sample of $(C_3H_6)_2Pt_2Cl_4$ (2455 ppm) in the same solvent. Finally, the orange solid had a 1H NMR spectrum (NT-360 MHz) as follows: δ 1.664 (d, 3H, J 6.03 Hz); 5.6 (m, 1H); 4.7 (m, 1H); 4.5 (m, 1H) ppm.

The distillate, which was obtained from the low pressure removal of the solvent from the Speier catalyst solution (vide supra), contained acetone (IR band at 1715 cm^{-1}). Coinjection with authentic acetone on VPC (Carbowax 1540, capillary column ($150' \times 0.01''$)) confirmed this). Thus, the following reaction is firmly established (eq. 1).



This surprising transformation in which reduction-dehydration and complexation occurs with remarkable ease is not without precedent. Over a century ago, quite an analogous reaction was reported [11] (eq. 2). Also the formation of

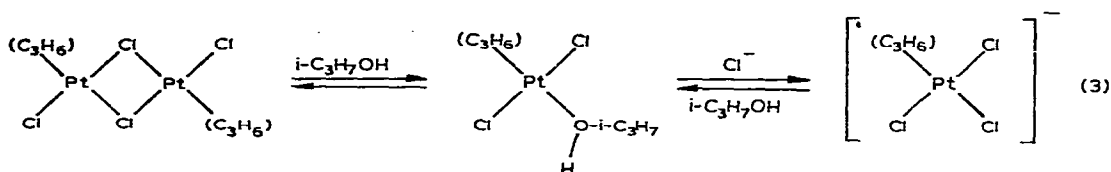


analogous Zeise compounds from alcohols is well known [12].

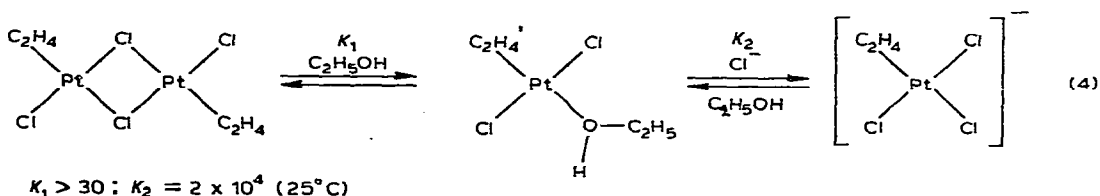
Of considerable importance was our observation that the yellow isopropyl alcohol solution of the authentic dimer, $(C_3H_6)_2Pt_2Cl_4$, gave a far-infrared spectrum with bands at 380(vs), 348(s), 328(w) and 304(m) cm^{-1} which was quite different both from Speier's catalyst solution (bands at 379(s), 328(vs) and 306(m) cm^{-1}) and from the Nujol mull spectrum of the orange solid. The latter we had proved to be the propyleneplatinum dimer (bands at 420(m), 396(s), 361(vs), 352(sh), 319(s), 288(s) and 237(m) cm^{-1}). The addition of small amounts of tetraethylammonium chloride dissolved in isopropyl alcohol to the authentic dimer [9] likewise dissolved in isopropyl alcohol resulted in a diminished intensity of the band at 348 cm^{-1} and the appearance of new bands

*In all of our work with Speier's catalyst, we refer to two-week-old catalyst as "aged". If freshly prepared catalyst is allowed to stand for two weeks, we have found that its activity seems to remain unchanged thereafter.

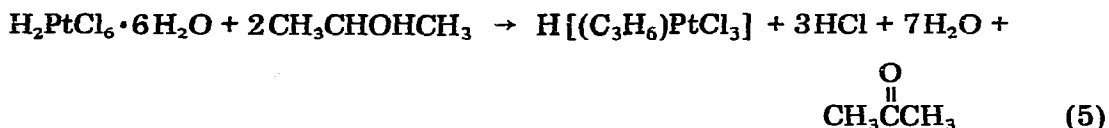
at 331 and 308 cm^{-1} . Further addition of the quaternary salt caused the band at 348 cm^{-1} to vanish and intensified the bands at 331 and 308 cm^{-1} . This strongly suggested that the following solvolysis sequence was occurring:



Thus, the absorption frequencies of the authentic dimer complex with excess chloride ion are in close agreement with both the Speier catalyst solution and of $\text{K}[(\text{C}_3\text{H}_6)\text{PtCl}_3] \cdot \text{H}_2\text{O}$ in Nujol [13]. The ease of solvolysis of platinum dimer complexes is well known [14].



In this connection it should be pointed out that solutions of the authentic dimer complex, $[(\text{C}_3\text{H}_6)\text{PtCl}_2]_2$ in pure acetone or isopropyl alcohol are not stable indefinitely, affording dark solutions or depositing black platinum precipitates within a day. Apparently, the attendant chloride ion liberated as a result of the chemical transformation shown in eq. 5 stabilizes the anionic platinum(II) complex. In our hands, a carefully prepared batch of catalyst was



stable up to 2.5 years in that it was still devoid of the black precipitate.

To summarize: "Speier's catalyst" contains the platinum complex, $\text{H}[(\text{C}_3\text{H}_6)\text{PtCl}_3]$, which, under hydrosilylation conditions, undergoes the catalytic cycle described by Chalk and Harrod [3]. This confirms previous observations: (1) Zeise compound, $(\text{C}_2\text{H}_4)_2\text{Pt}_2\text{Cl}_4$ gives the same results as the Speier catalyst in terms of rate, yields and products in hydrosilylations [3]; (2) Some differences have been noted between fresh and aged catalyst [15].

We plan to continue our investigation of the Speier catalyst and to make more precise the schematic mechanism of hydrosilylation as proposed by Harrod and Chalk [3].

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