Journal of Organometallic Chemistry, **160 (1978) 477—497**

Vinylmetallics as Ligands. VI.*
Preparation and Stabilities of a Series of Vinylsilane-Platinum(0) Complexes

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(Received April 4th, 1978)

Summary

A series of complexes of formula, $[(Ph_3P)_2PtCH_2{=}CHSi(CH_3)_n(OC_2H_5)_{3-n}]$ (n = 0,1,2,3), has been prepared and characterized. The all carbon compound, $[(Ph_3P)_2PtCH_2{=}CHC(CH_3)_3]$, has also been prepared and found to decompose in solution much more readily than its silicon analogue.

Introduction

In 1957 Chatt, Rowe and Williams reported the discovery of a stable series of acetylene complexes of formula, $[(PPh_3)_2Pt(ac)]$ (ac = acetylene)[1], and a similar unstable series of olefin complexes. At about the same time Malatesta and Cariello reported the synthesis of the related compounds, $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_4]$.[2] Since that time interest in the

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*For Part V, see Ref. 9.

coordination chemistry of platinum(O) has grown, and a considerable number of olefin- and acetylene-platinum(O) complexes have been prepared and characterized.[3,4] As originally noted by Chatt and co-workers[1,5] complexes of acetylenes, $[(PPh_3)_2Pt(ac)]$, are more stable than those of corresponding olefins, $[(PPh_3)_2Pt(ol)]$ (ol = olefin), and electron withdrawing substituents attached to the unsaturated ligands are effective in increasing stability in both cases. Hartley has noted from observation of decomposition points that thermal stability in complexes of the type, $[(PPh_3)_2Pt(X_2C{=}CX_2)]$, decreases in the order $X = CN > F > H$.[4]

Calorimetric measurements have shown that the platinum-olefin bond in $[(PPh_3)_2Pt(TCNE)]$ (TCNE = tetracyanoethylene) is 156 $kJmol^{-1}$ more stable than that in $[(PPh_3)_2Pt(CH_2{=}CH_2)]$,[6] and that the platinum-diphenylacetylene bond in $[(PPh_3)_2Pt(PhC{\equiv}CPh)]$ is about 82 $kJ\ mol^{-1}$ more stable than that in the ethylene complex.[7] These data further suggest that increased stability in platinum(0) compounds is associated with unsaturated ligands which are electron deficient.

Since the trimethylsilyl group has been shown to have a net electron withdrawing effect when attached to a carbon-carbon multiple bond,[8] and since electronic effects in π-bonded ligands seem to be of importance in determining stability in both platinum(0) and platinum(II) complexes, it became desirable to determine if vinylsilanes could function as ligands in compounds of the type, $[(PPh_3)_2Pt(ol)]$. We have reported the synthesis of $[(PPh_3)_2PtCH_2{=}CHSi(CH_3)_3]$ in a preliminary communication;[9] we now wish to report on the preparation and characterization of a series of complexes of formula, $[(PPh_3)_2PtCH_2{=}CHSi(CH_3)_n(OC_2H_5)_{3-n}]$ where n = 0,1,2,3.

Experimental

General

All syntheses of vinylsilane-platinum(0) complexes were conducted in an atmosphere of argon. IR spectra were determined using a Beckman IR-10 Spectrophotometer. Solid samples were analyzed as KBr wafers while liquid samples were analyzed as solutions in carbon tetrachloride or benzene. All spectra were calibrated against the 1601 cm^{-1} band of polystyrene. Proton NMR spectra were recorded in benzene-d_6 on a Perkin Elmer Model R-12A spectrometer. Carbon and Hydrogen were either determined locally on a Coleman Model 33 Analyzer, or were determined by Galbraith Laboratories, Knoxville, Tennessee. Mass spectra were determined with a Varian Em-600 Mass Spectrometer. Visible and ultraviolet spectra were recorded on a Coleman 124 Double Beam Spectrometer.

The unsaturated silanes used were obtained commercially, and their purity was checked by gas chromatography. Vinylmethyldiethoxysilane, which was found to be contaminated with a small amount of halosilane, was purified by fractional distillation

Table 1

Properties of Complexes of Type $(PPh_3)_2Pt(ol)$

Olefinic ligand (ol)	No.	Yield(%)	m.p.°	Color	%C (calcd)	%H (calcd)
$CH_2=CHSi(CH_3)_3$	2	96	140-142	White	60.06 (60.06)	5.51 (5.16)
$CH_2=CHSi(CH_3)_2(OC_2H_5)$	3	78	137-8d	White	59.40 (59.35)	5.56 (5.22)
$CH_2=CHSi(CH_3)(OC_2H_5)_2$	4	51	91d	White	58.07 (58.69)	5.47 (5.27)
$CH_2=CHSi(OC_2H_5)_3$	5	72	131-2d	White	57.73 (58.08)	5.62 (5.32)
$CH_2=CHC(CH_3)_3$	6	48	110-112d	Off White	62.53 (62.75)	5.70 (5.27)

after having been refluxed with absolute alcohol for one hour. The hydrocarbon, 3,3-dimethyl-1-butene, was also obtained commercially and was used without further purification. The compounds, trans-4,4'-dinitrostilbene[10] (Found: C, 62.20; H, 4.16. $C_{14}H_{10}N_2O_4$ calcd.: C, 62.21; H, 3.72%) and bis(triphenylphosphine)-(ethylene)platinum(0)[4] (Found: C, 61.04; H, 5.00. $C_{38}H_{34}P_2Pt$ calcd.: C, 61.04; H, 4.58% m.p. = 125-127° lit.[11] m.p. = 122-125°) were prepared according to published procedures.

Technical grade hexane was first shaken with conc. sulfuric acid several times to remove olefinic impurities. It was then washed with dil. sodium bicarbonate, dried by refluxing over calcium hydride, distilled and stored over Linde molecular sieves (Type 4A, 1/16"). Benzene was dried in a similar manner.

Analytical data for all new compounds are collected in Table 1.

Synthesis

Bis(triphenylphosphine)(vinyltrimethylsilane)-platinum(0).[9] In a typical preparation, a solution of $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ (1.00 g, 1.34 mmol) in benzene (22 ml) was saturated with argon. The solution was filtered and excess vinyltrimethylsilane (5 ml) added. The mixture was stirred for 15 minutes at ambient temperature. The reaction mixture was then frozen and partially evacuated. When thawed, the reaction mixture was stirred under partial vacuum for 15 minutes. The freezing, pumping, thawing and stirring process was repeated twice after which the solvent and excess ligand were removed in vacuo to leave $[(PPh_3)_2Pt(CH_2{=}CH)Si(CH_3)_3]$ as a white powder which was washed with hexane and dried in vacuo. Yields as high as 96% (1.06 g) have been obtained, and the complex is stable for hours in air and for days under argon. Selected IR bands: 819, 835, 1245(sh), 1262 cm^{-1}.

Bis(triphenylphosphine)(vinyldimethylethoxysilane)-platinum(0). In a manner analogous to that described above $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ (0.90 g, 1.21 mmol) was allowed to react with excess vinyldimethylethoxysilane (5 ml) in benzene (20 ml) solution to yield upon stripping the solvent a brown viscous oil. The oil was crystallized by adding hexane (20 ml), cooling to -78° and stirring briskly whereupon it gradually changed to a white powder which was isolated by filtration, washed with hexane and dried in vacuo to yield 0.80 g (78%) of $[(PPh_3)_2Pt(CH_2{=}CH)Si(CH_3)_2(OC_2H_5)]$. The IR spectrum of the complex shows no change even after the complex has stood in air for 20 hours. Selected IR bands: 815, 930 1085, 1245, 1255(sh) cm^{-1}.

Bis(triphenylphosphine)(vinylmethyldiethoxysilane)-platinum(0). In a manner analogous to that described above $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ (1.00 g, 1.34 mmol) was allowed to react with excess vinylmethyldiethoxysilane

(5 ml) in benzene (22 ml) solution. The brown viscous substance originally obtained was once again converted to a white solid, $[(PPh_3)_2Pt(CH_2{=}CH)Si(CH_3)(OC_2H_5)_2]$, upon cooling and stirring with hexane in 51% yield (0.60 g). Selected IR bands: 800, 920, 1075, 1250, 1265 cm^{-1}.

Bis(triphenylphosphine)(vinyltriethoxysilane)-platinum(0). In a manner analogous to that described above $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ (1.00 g, 1.34 mmol) was allowed to react with excess vinyltriethoxysilane (5 ml) in benzene (22 ml) solution. Stripping the solvent left the desired complex suspended in excess vinyltriethoxysilane from which it is separated by washing with hexane followed by drying in vacuo. The white solid, $[(PPh_3)_2Pt(CH_2{=}CH)Si(OC_2H_5)_3]$ is obtained in 72% yield (0.87 g). Selected IR bands: 955, 1090 cm^{-1}.

Bis(triphenylphosphine)(3,3-dimethyl-1-butene) platinum(0). In a manner analogous to that described for the preparation of the vinyltrimethylsilane complex, $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ (1.00 g, 1.34 mmol) was allowed to react with a large excess (15 ml) of 3,3-dimethyl-1-butene in benzene (20 ml). After the freezing and stirring in a partial vacuum routine had been repeated three times the reaction mixture was concentrated in vacuo to a small volume (3-5 ml). A de-gassed solution comprised of hexane (30 ml) and 3,3-dimethyl-1-butene (3 ml) was added to the reaction and the initially formed precipitate was isolated by filtration and discarded. The filtrate was again concentrated _in vacuo_ and treated with an argon saturated mixture of hexane (20 ml) and 3,3-dimethyl-1-butene (3 ml). The off-white precipitate, $[(PPh_3)_2Pt(CH_2=CH)C(CH_3)_3]$, which was collected and dried _in vacuo_ for 45 minutes was obtained in 48% yield (0.52 g) A mass spectrum of the volatiles resulting from pyrolysis of the complex at 160° indicated the presence of 3,3-dimethyl-1-butene.

Bis(triphenylphosphine)(trans-4,4'-dinitrostilbene)-platinum(0). $[(PPh_3)_2Pt(CH_2=CH_2)]$ (1.20 g, 1.61 mmol) was dissolved in benzene (23 ml) to give a solution which was de-gassed, filtered, and saturated with argon. Trans-4,4'-dinitrostilbene (0.64 g, 2.37 mmol) suspended in dry benzene (25 ml) was added to the stirred solution of the ethylene complex. The mixture was again degassed and heated to 50° for 35 minutes. After it cooled to room temperature the mixture was filtered. The solvent was then removed _in vacuo_ from the red filtrate. Ethanol (5 ml) was added to the residue and the orange-red precipitate which was isolated by filtration was washed with hexane and dried _in vacuo_. The yield of $[(PPh_3)_2Pt(O_2NC_6H_4CH=CHC_6H_4NO_2)]$ was 1.10 g (69.2%), and it melted at 204-205° (lit. 204-205°).[5] (Found: C, 61.01; H, 4.31. $C_{50}H_{40}N_2O_4P_2Pt$ calcd.: C, 60.75; H, 4.05%).

Determination of Equilibrium Constants

Beer's Law Data for Bis(triphenylphosphine)(trans-4,4'-dinitrostilbene)platinum(0). Fifteen samples of the trans-4,4'-dinitrostilbene complex were weighed separately, and each was then placed in a 25 ml volumetric flask which was then closed with a serum cap, evacuated and filled with argon. Argon-saturated, dry toluene was added to make up the total volume of 25 ml; the complex was dissolved by vigouous shaking; an aliquot was transferred to a serum-capped, argon-filled 1 cm cuvette, and the absorbance at 420 nm was measured within 10 minutes of preparing the samples. The concentrations of the solutions ranged from 13.4 x 10^{-5}M to 1.75 x 10^{-5}M and the corresponding absorbances ranged from 1.77 to 0.21 respectively. A least squares analysis of the absorbance data yielded the relation, $A = 1.47 \times 10^4\ C + 6.86 \times 10^{-4}$ where A = absorbance and C = concentration in moles/l. The computed correlation coefficient, r, is equal to 0.96.

Displacement of Trans-4,4'-Dinitrostilbene From Its Bis(triphenylphosphine)Platinum(0) Complex by Vinylsilanes. Stock solutions of the vinylsilane ligands studied were prepared in argon-saturated, dry toluene with the careful exclusion of air. Several samples of solid bis(triphenylphosphine)(trans-4,4'-dinitrostilbene)-platinum(0) were then weighed separately, and each was placed in a 25 ml volumetric flask which was then closed with a serum cap, evacuated and filled with argon. From this point each sample was handled individually.

About 20 ml of toluene was added by means of a syringe; the complex was dissolved by vigorous shaking, and then a known volume of the stock vinylsilane solution was added. The sample was then diluted to volume and mixed thoroughly, after which the absorbance measurement at 420 nm was made.

Because the solutions decompose on standing all absorbance measurements were made within ten minutes of mixing. Equilibrium constants were then calculated using the relation shown under equation (3). Experimental results used in the calculation of K for each ligand follow. In each instance the first concentration given is the initial concentration of $[(PPh_3)_2Pt(DNS)]$, the second concentration given is the intial concentration of the vinylsilane ligand and the third number is the absorbance measured for the mixture in a 1 cm quartz cuvette

a.) Vinyltrimethylsilane - Run 1, 1.23 x 10^{-4}M, 4.29 x 10^{-2}M, 0.77; Run 2, 1.09 x 10^{-4}M, 2.10 x 10^{-2}M, 0.94; Run 3, 1.10 x 10^{-4}M, 2.14 x 10^{-2}M, 0.97; Run 4, 1.14 x 10^{-4}M, 3.22 x 10^{-2}M, 0.82; Run 5, 1.16 x 10^{-4}M, 3.53 x 10^{-2}M, 0.84.

b.) Vinyldimethylethoxysilane - Run 1, 1.11 x 10^{-4}M, 2.28 x 10^{-2}M, 0.47; Run 2, 1.17 x 10^{-4}M, 3.05 x 10^{-2}M, 0.43; Run 3, 1.07 x 10^{-4}M, 1.52 x 10^{-2}M, 0.56; Run 4, 1.09 x 10^{-4}M, 1.51 x 10^{-2}M, 0.56.

c.) Vinylmethyldiethoxysilane - Run 1, 1.16 x 10^{-4}M, 2.06 x 10^{-2}M, 0.34; Run 2, 1.17 x 10^{-4}M, 2.75 x 10^{-2}M, 0.28; Run 3, 1.14 x 10^{-4}M, 1.37 x 10^{-2}M, 0.44; Run 4, 1.07 x 10^{-4}M, 1.37 x 10^{-2}M, 0.41; Run 5, 1.01 x 10^{-4}M, 6.83 x 10^{-3}M, 0.58.

d.) Vinyltriethoxysilane - Run 1, 1.05 x 10^{-4}M, 5.75 x 10^{-3}M, 0.59; Run 2, 1.07 x 10^{-4}M, 1.15 x 10^{-2}M, 0.41; Run 3, 1.07 x 10^{-4}M, 1.15 x 10^{-2}M, 0.40; Run 4, 9.56 x 10^{-4}M, 5.75 x 10^{-3}M, 0.54; Run 5, 1.13 x 10^{-4}M, 1.73 x 10^{-2}M, 0.33.

Measurements were made at ambient temperature (22±2°C) and results are presented in Table 2.

Displacement of Vinyltriethoxysilane From Its Bis(triphenylphosphine)platinum(0) Complex by trans-4,4'-Dinitrostilbene. A stock solution of trans-4,4'-dinitrostilbene in toluene (0.005475 g in 200 ml) was prepared. Similarly, a stock solution of vinyltriethoxysilane in toluene (0.3602 g in 10 ml) was also prepared. Finally, several samples of the complex, $[(PPh_3)_2PtCH_2{=}CHSi(OC_2H_5)_3]$, were weighed into 25 ml volumetric flasks. Measured aliquots of the two stock solutions of the competing ligands were then added to the volumetric flasks containing the platinum complex, the solutions were mixed, and the absorbance was measured at 420 nm. The average calculated value of the equilibrium constant is shown in Table 2 and the experimental results are shown below. The first number in each run corresponds to the initial concentration of $[(PPh_3)_2Pt(CH_2{=}CH)Si(OC_2H_5)_3]$; the second number is the initial concentration of free $(CH_2{=}CH)Si(OC_2H_5)_3$; the third number is the initial concentration of free 4,4'-dinitrostilbene, and the last number represents the observed absorbance - Run 1, 8.07 x 10^{-5}M, 7.57 x 10^{-3}M,

Table 2

Equilibrium Constants for the Formation of Platinum(0)-Vinylsilane Complexes from$[(PPh_3)_2Pt(DNS)]$

No.	Complex	K^1
2	$[(PPh_3)_2PtCH_2{=}CHSi(CH_3)_3]$	$1.73 \pm 0.31 \times 10^{-3}$
3	$[(PPh_3)_2PtCH_2{=}CHSi(CH_3)_2(OC_2H_5)]$	$8.60 \pm 0.28 \times 10^{-3}$
4	$[(PPh_3)_2PtCH_2{=}CHSi(CH_3)(OC_2H_5)_2]$	$1.68 \pm 0.17 \times 10^{-2}$
5	$[(PPh_3)_2PtCH_2{=}CHSi(OC_2H_5)_3]$	$1.93 \pm 0.19 \times 10^{-2}$ $(2.53 \pm 0.46 \times 10^{-2})^2$

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[1] Reported values of K are averages of five (four in the case of 3) independent determinations (T=22±2°).

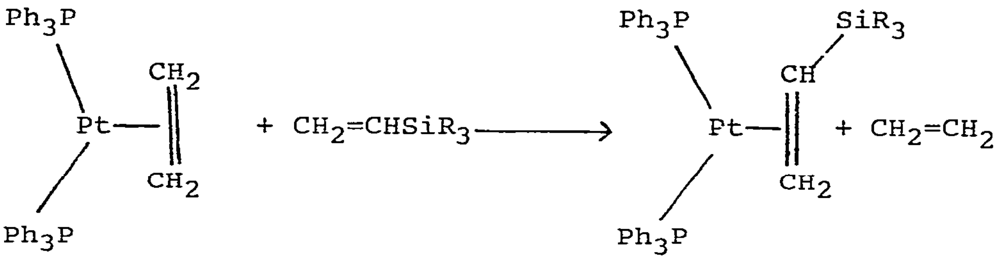
[2] Average of six independent measurements - approach to equilibrium from the opposite direction by reaction of DNS with 5.

9.72×10^{-5}M, 0.39; Run 2, 1.17×10^{-4}M, 7.57×10^{-3}M, 9.72×10^{-5}M, 0.48; Run 3, 9.96×10^{-5}M, 7.57×10^{-3}M, 9.72×10^{-5}M, 0.37; Run 4, 5.96×10^{-5}M, 3.79×10^{-3}M, 9.93×10^{-5}M, 0.39; Run 5, 4.84×10^{-5}M, 3.79×10^{-3}M, 9.93×10^{-5}M, 0.29; Run 6, 3.28×10^{-5}M, 3.79×10^{-3}M, 9.93×10^{-5}M, 0.21.

Results and Discussion

Preparation and Characterization

Of the several reported routes to the synthesis of complexes of the type, $[(PPh_3)_2Pt(ol)]$,[4] we have found the displacement of ethylene from bis(triphenylphosphine)-(ethylene)platinum(0) (compound 1) to be most satisfactory for the preparation of vinylsilane complexes (Eq. 1).



(1)

$R = -CH_3$ and/or $-OC_2H_5$

The reactions were performed under a partial vacuum with occasional removal of ethylene to drive the reaction toward formation of the desired complex. Some of the properties of the compounds prepared are summarized in Table 1.

The preparation of 6, which is the all carbon analogue of the vinyltrimethylsilane complex, 2, required the presence of a large excess of 3,3-dimethyl-1-butene throughout the entire procedure, including washings, to prevent the dissociation of the complex during isolation.

All of the vinylsilane complexes prepared are insoluble in hexane but somewhat soluble in benzene. They react, as expected, with halogenated solvents such as chloroform or carbon tetrachloride.[12] Although stable to brief exposure to air they are best stored in an inert atmosphere. The presence of ethoxy groups improves this stability as evidenced by the observation that the IR spectrum of the vinyldimethylethoxysilane complex did not change even after the complex had stood in air for 20 hours.

The vinylsilane-platinum(0) complexes have been observed to be much more stable to cleavage of the silicon to vinylic carbon bond than their platinum(II) analogues. For example, the ^1H NMR spectrum of a wet acetone-d_6 solution of 2 showed no change in any signal intensities during a 24 hour period. In contrast, $K[PtCl_3(CH_3)_3SiCh{=}CH_2]$, under similar conditions, undergoes extensive decomposition to form $K[PtCl_3(CH_2{=}CH_2)]$ and hexamethyldisiloxane.[13] Similar results over a 14 hour period for 5 can also be contrasted with the behaviour of $K[PtCl_3(C_2H_5O)_3SiCH{=}CH_2]$ which is extensively hydrolyzed within minutes in wet acetone-d_6.[14] These results might have been anticipated since the backbonding in platinum(0) likely dominates the interaction of this species with olefins and likely prevents facile Si-C bond cleavage in the coordinated ligand.

Finally, exchange between coordinated and free vinylsilane ligands in the platinum(0) series studied must be slow on the NMR time scale since benzene-d_6 solutions containing either $\underline{\underline{2}}$ and free $CH_2{=}CHSi(CH_3)_3$ or $\underline{\underline{5}}$ and free $CH_2{=}CHSi(OC_2H_5)_3$ showed unshifted resonances assignable to both the coordinated and uncoordinated ligands. Tolman and co-workers have recently reported similar results for the ethylene complex.[15]

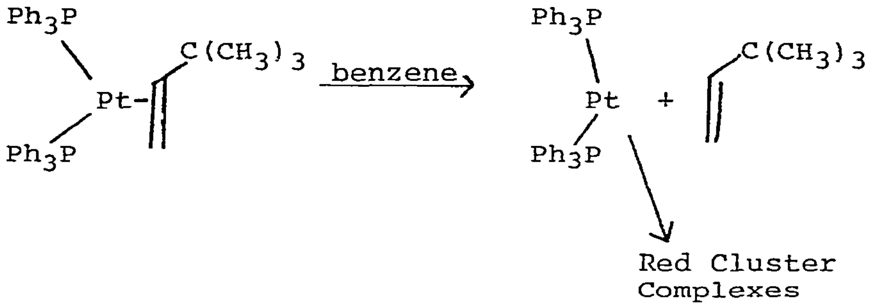
Spectra

The infrared spectra of the complexes were dominated by bands assignable to the triphenylphosphine ligand vibrations. However, bands involving Si-C and Si-O-C vibrations prove useful for quick identification of the complexes in reaction mixtures, and these are included in the experimental section.

All NMR spectra obtained were initially referenced to the proton impurity in the benzene-d_6 solvent (δ7.24) because tetramethylsilane (TMS) has a peak which is overlapped by the Si-CH_3 peak in the complexes. The peak assigned to resonance of the complexed vinyl group was observed to be poorly resolved and weak in each of the compounds studied reflecting the limited solubility of the complexes and extensive ^{195}Pt-^{1}H coupling.

However, the centers of the multiplets could be estimated and these were observed at δ2.7 in 2, δ2.6 in 3, δ2.5 in 4 and δ2.5 in 5. For purposes of comparison, the center of the olefinic resonance in $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ is reported at δ2.59[15] and the vinyl resonance is centered at δ5.9 in $CH_2{=}CHSi(CH_3)_3$ and at δ4.2 in $K[PtCl_3(CH_3)_3Si(CH{=}CH_2)]$.[13] It is likely that the large upfield shift in the platinum(0) complexes reflects, at least in part, the high electron density which must be born by the olefin in complexes of the type, $[(PPh_3)_2Pt(ol)]$ although local field anisotropy might also be responsible for part of the effect. It should be noted in passing that two methyl resonances were observed in the spectrum of 3 (δ0.07 and δ0.13) as expected since the molecule is diastereotopic. Similar results are observed for the ethoxy groups in 4.

Unfortunately, the NMR spectrum of 6, the all carbon analogue of 2, has not been observed because 6 instantly decomposes to give deep red solutions when dissolved in benzene. The spectra of these red solutions indicate very poorly resolved multiplets at δ2.7 and δ5.0 ppm which might arise from coordinated and free 3,3-dimethyl-1-butene. In addition, the samples contain the expected singlet at δ1.0 ppm expected from the t-butyl group. The deep red solutions which form are reminiscent of Ugo's red cluster compounds[16] and could possibly result from a decomposition such as that shown in equation (2) below.



(2)

It is known that xylene solutions of $[(PPh_3)_2Pt(CH_2{=}CH_2)]$ form cluster complexes when nitrogen is bubbled through them for 24 hours.[17]

Equilibrium Measurements

The equilibrium constant, K, for reaction (3) shown below has been estimated in toluene solution,

$$CH_2{=}CH{-}SiR_nR'_{3-n} + (PPh_3)_2Pt(DNS) \rightleftharpoons (PPh_3)_2PtCH_2{=}CHSiR_nR'_{3-n} + DNS \qquad (3)$$

where $R = -CH_3$

$R' = -OC_2H_5$

DNS= 4,4'-Dinitrostilbene

$$K = \frac{[(PPh_3)_2Pt(\text{silane})][DNS]}{[\text{silane}][(PPh_3)_2Pt(DNS)]}$$

and the results are shown in Table 2. The 4,4'-dinitrostilbene complex, 7, was chosen as the reference compound to which the stabilities of the vinylsilane complexes were compared for several reasons. In the first place 7 absorbs rather strongly at 420 nm ($\varepsilon = 1.47 \pm .10 \times 10^4$)

and is the only species showing significant absorption at that point. Thus it can be used as the basis for a spectrophotometeric determination of K for reaction (3). In addition, 7 is easily prepared and keeps well in the solid state. On the other hand, toluene solutions of 7 do slowly decompose on standing, and for this reason all measurements were made as soon after mixing as practicable (within 10 minutes). It is for this reason also that all measurements were made at ambient temperature. For compound 5 the equilibrium was approached from both the forward and reverse directions (see equation 3) to give results which are identical within experimental error (see Table 2).

The equilibrium constants listed in Table 2 indicate that the vinylsilane complexes are all considerably less stable than the dinitrostilbene complex. This is to be expected considering the strong acceptor properties of the nitro group compared to the electropositive nature of silicon.

As might be anticipated the incorporation of the electron-attracting ethoxy group into the vinylsilane ligand increases the stability of the platinum(0) complex, presumably by increasing the π-acceptor ability of the ligand. As can be seen in Table 2 there is about one order of magnitude change in the value of K in going from the $-Si(CH_3)_3$ group to the $-Si(OC_2H_5)_3$ group. This stability increase parallels the qualitatively observed air stability of the complexes.

Conclusions

The contrast between the qualitative stability of $[(PPh_3)_2PtCH_2{=}CHSi(CH_3)_3]$, 2, compared to that of its carbon analogue, $[(PPh_3)_2PtCH_2{=}CHC(CH_3)_3]$, 6, is striking. Quantitiative measurements of the solution stability of 6 are precluded because of its very rapid decomposition upon dissolution in benzene or toluene.

It should be noted that the steric requirement for coordination of the 3,3-dimethyl-1-butene ligand might be expected to be more stringent than for vinyltrimethylsilane because of the difference in the radii of C and Si. However, crowding around the double bond does not prevent the existence of the compound, 1,3-dichloro -2-(3,3-dimethyl-1-butene)-4-(2,4,6-trimethylpyridine)platinum(II), which is known, and which has not been reported to be unstable.[18] One would expect therefore that in the nearly trigonal phosphine-platinum(0) complexes that steric requirements of the lagands should be no more rigorous than in the platinum(II) complex.

On the other hand, electronic factors may explain the difference in stability. It is well known that platinum(0)-olefin complexes are stablized by electron-withdrawing ligands which enhance the apparently all important platinum to olefin backbonding.[4] One might therefore argue that the vinylsilane complexes are stablized, compared to the 3,3-dimethyl-1-butene complex, through a mechanism which enhances their ability to accept back-donated electron density from the platinum atom such as an interaction between the π^* orbital of the olefin and a d-orbital of suitable symmetry on the silicon atom. The observed equilibrium constant data for ethoxy-substituted vinylsilane complexes are consistent with this idea.

Acknowledgement

The authors are pleased to acknowledge the support of this work by the Robert A. Welch Foundation (Grant No. AI-306).

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