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Catalysis of hydrosilylation Part XVIII.* $Pt(PPh_3)_2(CH_2=CH_2)$ — a versatile catalyst for hydrosilylation of olefins

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$Pt(PPh_3)_2(CH_2=CH_2)$ appeared to be a versatile catalyst in hydrosilylation of alkenes (with 5–22 C atoms) as well as of functionalized alkenes such as allyl chloride, allylamine, allyl methacrylate and vinylsilanes. In comparison with a well-known Speier catalyst or with $Pt(PPh_3)_4$, this complex is characterized by a very high effectiveness (activity and selectivity) and relative resistance to oxygenation and it may be applied in recycling runs with a minor induction period. The catalytic processes examined are of great industrial importance since they lead to a synthesis of alkylsilanes, disilylethanes and silane coupling agents.

Keywords: hydrosilylation, homogeneous catalysis, platinum complex, trisubstituted silanes, olefins

INTRODUCTION

Most research and industrial syntheses of organosilicon compounds based on hydrosilylation are carried out in the presence of platinum complexes. Hexachloroplatinic acid (H_2PtCl_6), usually dissolved in an organic solvent, e.g. isopropyl alcohol (the Speier catalyst), has appeared to be the most common precursor of, mainly, the Pt(II) catalyst, although in the presence of hydrosilane a reduction of Pt(IV), even to Pt(0) species, is observed.[1–4] Therefore, some attempts have been made to apply Pt(0) complexes as direct catalysts of hydrosilylation, namely $Pt(PPh_3)_4$[5–9] and, more recently, $Pt(PPh_3)_2$(olefin) (where olefin refers mainly to $CH_2=CH_2$[10,11]) or $Pt(PR_3)_2[(CH_2=CHSiMe_2)_2O]$[12] and $Pt(PPh_3)_2[(EtO)_3SiCH=CH_2]$.[13]

This replacement has aimed at avoiding or shortening the induction period which characterizes H_2PtCl_6–solvent catalytic systems. Besides, many hydrosilylation reactions are not effectively catalysed by these systems.

$Pt(PPh_3)_2(CH_2=CH_2)$ was reported previously to have been used efficiently only in the hydrosilylation of 1-hexene and trimethylvinylsilane by (alkyl, chloro)silane and diethylsilane.[10,11] Our experience in catalysis of hydrosilylation by platinum complexes led us to apply the above complex as a versatile catalyst for many processes for hydrosilylation of the C=C bond, particularly by trichlorosilane, methylchlorosilanes and trialkoxysilanes. These processes have an industrial importance because they lead to synthesis of silane coupling agents as well as alkyltri(chloro, alkoxy)silanes and disilylethanes.

RESULTS AND DISCUSSION

$Pt(PPh_3)_2(CH_2=CH_2)$ (complex **I**) was tested in the following hydrosilylation reactions:

(a) 1-octene and 1-octadecene with trisubstituted silanes [Me_2ClSiH, $MeCl_2SiH$, Cl_3SiH and $(EtO)_3SiH$];
(b) allyl chloride with trichlorosilane;
(c) allylamine with triethoxysilane;
(d) allyl methacrylate with trichlorosilane and triethoxysilane;
(e) vinyltriethoxysilane with triethoxysilane.

The Speier catalyst as well as, in some cases, $Pt(PPh_3)_4$ and other common platinum catalysts were used as references in all catalytic experiments.

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Hydrosilylation of 1-octene and 1-octadecene

The above alkenes were chosen (from a series of C_5-C_{22} alkenes) to test complex **I** since the products of their hydrosilylation are of practical importance; i.e. octadecyl- and octyl-substituted silanes are commonly used in the modification of inorganic materials, e.g. silicas as supports for HPLC, as agents for hydrophobization or as monomers or co-monomers for synthesis of organosilicon polymers and modification of organic polymers.

The reaction occurs according to Eqn [1].

Detailed results on the hydrosilylation of 1-octene are compiled in Table 1.

An advantage of the complex **I** is its practically 100% selectivity of hydrosilylation products. Contrary to Speier catalysts,[14] complex **I** does not catalyse the redistribution of the silane. Besides, while at room temperature (298 K) the Speier catalyst appeared to be more effective (except for the reaction of 1-octene with Cl_3SiH), at 323 K complex **I** is generally more active and obviously more selective than the Speier catalyst (except for the reaction of 1-octene with dimethylchlorosilane).

The results for hydrosilylation of 1-octadecene compiled in Table 2 testify to the higher effectiveness of complex **I** compared with the Speier and $Pt(PPh_3)_4$ catalysts in the hydrosilylation for all the trisubstituted silanes examined. However, on the basis of the above results, no general rule can be formulated concerning the substituent effect at the silicon on the yield of the hydrosilylation products.

Hydrosilylation of allyl chloride

3-Chloropropyltrichlorosilane, synthesized according to the reaction of Eqn [2]:

and 3-chloropropyltrialkoxysilanes (formed from the alcoholysis of the previous species) are key silanes used for the industrial production of various carbofunctional silanes, e.g. A-1100, Si-69, A-1120, A-189, etc.[15]

Hydrosilylation of allyl chloride occurs in the presence of the majority of platinum complexes. The reaction is mostly carried out without solvent under reflux of the reagents from 312 K to *ca* 363 K in air

$$CH_3(CH_2)_nCH{=}CH_2 + HSiX_3 \xrightarrow{\text{catalyst}} CH_3(CH_2)_{n+2}SiX_3 \qquad [1]$$

$$n = 5{,}15;\ X_3 = Me_2Cl,\ MeCl_2,\ Cl_3,\ (EtO)_3$$

$$HSiCl_3 + CH_2{=}CHCH_2Cl \xrightarrow{\text{catalyst}} Cl_3SiCH_2CH_2CH_2Cl \qquad [2]$$

Table 1 Yield of n-octyl trisubstituted silanes (%) in the reaction of trisubstituted silanes with 1-octene catalysed by platinum complexes

Silane	Temp. (K)	Catalyst					
		$Pt(PPh_3)_2(CH_2{=}CH_2)$			H_2PtCl_6 (i-PrOH)		
		6h	15h	30h	6h	15h	30h
Me_2ClSiH	298	—	2–3	6	87	87	—
$MeCl_2SiH$	298	—	24	63	85(5)[a]	75(9)[a]	—
Cl_3SiH	298	90	91	89	84(8)[a]	78(14)[a]	—
$(EtO)_3SiH$	298	—	13	21	48	58	66
		2h	4h	6h	2h	4h	6h
Me_2ClSiH	323	34	37	66	73	66	76
$MeCl_2SiH$	323	72	75	79	65(9)[a]	62(9)[a]	71(8)[a]
Cl_3SiH	323	76	82	80	59(4)[a]	72	60(8)[a]
$(EtO)_3SiH$	323	89	83	85	26	44	47

$[\equiv SiH]:[\,{>}C{=}C{<}\,]:[\text{cat.}] = 1:1:10^{-3}$; air, glass ampoules.

[a] ( ), By-products.

Table 2 Yield of octadecyl trisubstituted silanes (%) in the reaction of trisubstituted silanes with 1-octadecene catalysed by platinum complexes

	Catalyst		
Silane	$Pt(PPh_3)_2(CH_2=CH_2)$	$Pt(PPh_3)_4$	H_2PtCl_6(i-PrOH)
Me_2ClSiH	80	0	59
$MeCl_2SiH$	77	54	52
Cl_3SiH	50	0	45
$(EtO)_3SiH$	83	60	30

$[\equiv SiH]:[\rangle C=C\langle]:[cat.] = 1:1:10^{-3}$; 353 K, 6 h, air, glass ampoules.

at atmospheric pressure. Under such conditions, the maximum yield of the main product is predominantly around 68 ± 6%.[3] As by-products, propyltrichlorosilane (~5%), $SiCl_4$ (5–10%) and siloxanes are usually recorded and they are accompanied by unreacted substrates: $HSiCl_3$ (3–5%) and allyl chloride (~10%).[16] Two positive effects were observed after the application of $Pt(PPh_3)_2(CH_2=CH_2)$ instead of using other well-known and active catalysts based on H_2PtCl_6: namely, a considerable shortening of the effective time of the reaction (Fig. 1; Table 3) (particularly after preliminary activation of the catalyst

Table 3 Effect of preliminary activation of $Pt(PPh_3)_2(CH_2=CH_2)$ by substrates on the yield of 3-chloropropyltrichlorosilane

Activation of catalyst	Yield of adduct (%)
No activation	62 (190)^a
$HSiCl_3$, reflux, 2 h, air	65 (45)
$HSiCl_3$, room temp, 2 h, air	63 (110)
$CH_2=CHCH_2Cl$, reflux, 2 h, air	68 (140)
$CH_2=CHCH_2Cl$, room temp. 2 h, air	50 (140)

$[Cl_3SiH]:[CH_2=CHCH_2Cl]:[cat.] = 1:1:2 \times 10^{-6}$.
[a] ( ) Time to reach the yield (min)

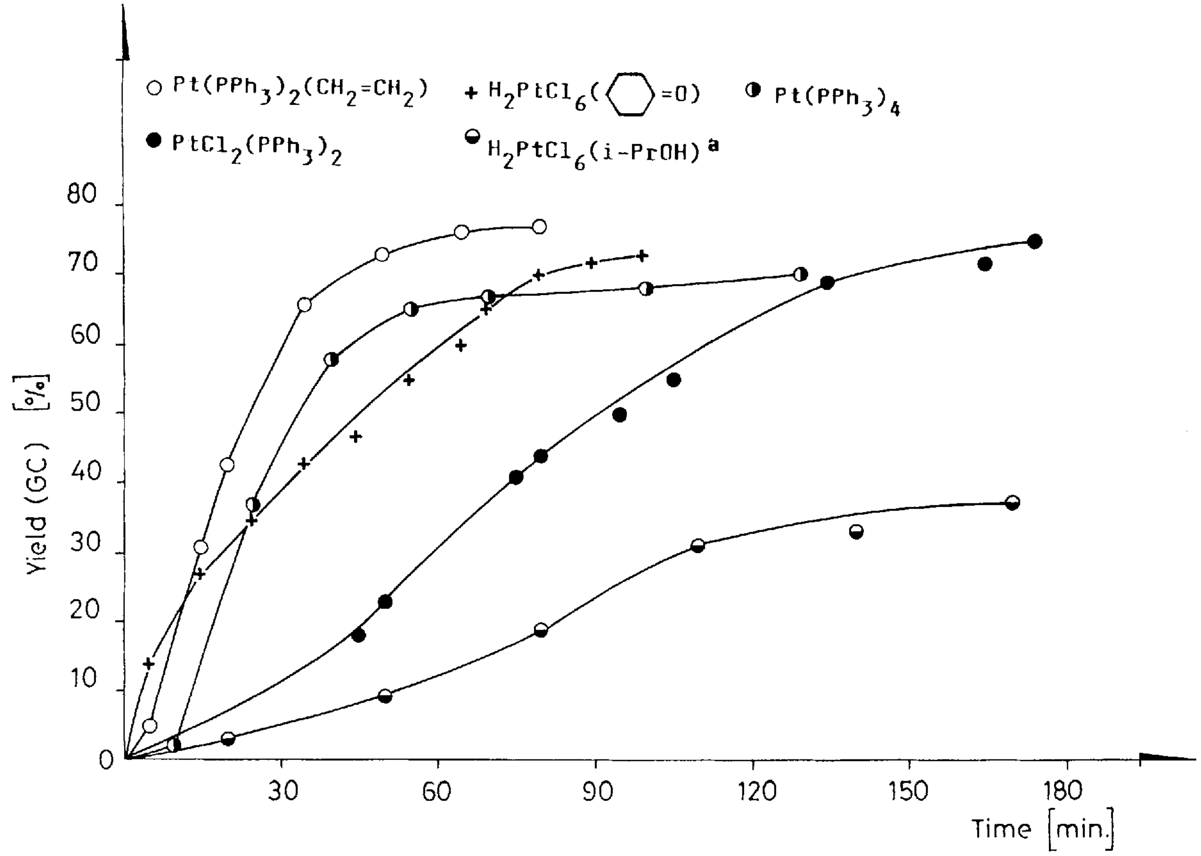


Figure 1 Effect of catalyst on the course of the hydrosilylation of allyl chloride by trichlorosilane: $[Cl_3SiH]:[CH_2=CHCH_2Cl]:[cat.] = 1:1:5 \times 10^{-6}$ ^{a} (10^{-4}); air, reflux.

by trichlorosilane under reflux conditions), as well as the possibility for a four-fold usage of the catalyst (see Table 4). Distillation of the 3-chloropropyltrichlorosilane *in vacuo* at a temperature below 373 K makes it possible to use the residual catalyst solution effectively in following runs.

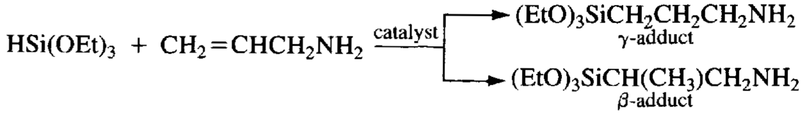
Table 4 Effect of the number of recycling runs on the yield of 3-chloropropyltrichlorosilane and time of reaching the stated yield

Recycling runs	Yield of adduct (%)
1	69 (45)[a]
2	71 (55)
3	70 (60)
4	74 (60)

$[Cl_3SiH]:[CH_2{=}CHCH_2Cl]:[cat.] = 1:1:5 \times 10^{-6}$; reflux, air.
[a] ( ) Time to reach the given yield (min).

Hydrosilylation of allylamine

The hydrosilylation reaction occurs according to Eqn [3]:



$$HSi(OEt)_3 + CH_2{=}CHCH_2NH_2 \xrightarrow{catalyst} \begin{cases} (EtO)_3SiCH_2CH_2CH_2NH_2 \quad \gamma\text{-adduct} \\ (EtO)_3SiCH(CH_3)CH_2NH_2 \quad \beta\text{-adduct} \end{cases} \qquad [3]$$

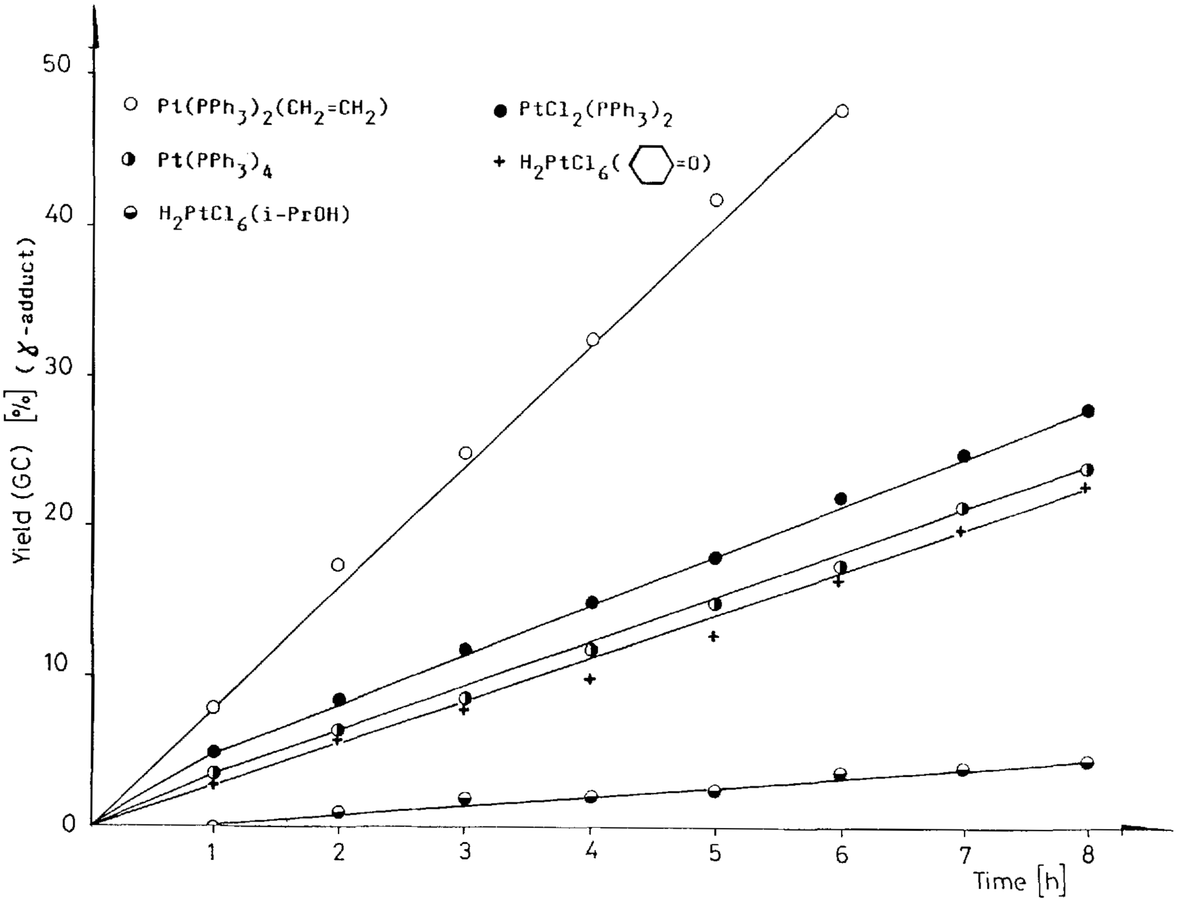
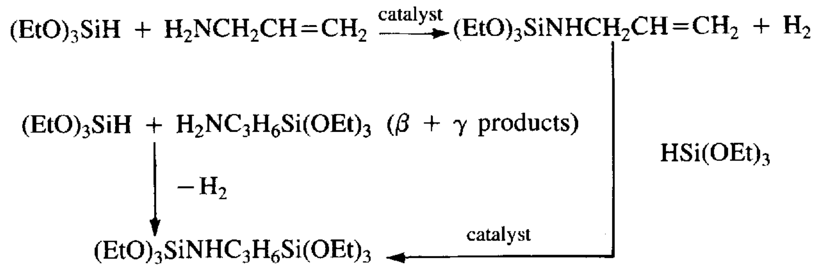


Figure 2 Effect of catalyst on the course of the hydrosilylation of allylamine by triethoxysilane: $[{\equiv}SiH]:[{>}C{=}C{<}]:[cat.] = 1:1:10^{-4}$; air, reflux.



[4]

$$(EtO)_3SiNHC_3H_6Si(OEt)_3 + EtOH \longrightarrow \underset{(\beta + \gamma)}{(EtO)_3SiC_3H_6NH_2} + (EtO)_4Si \quad [5]$$

The ratio of γ to β-adduct is predominantly around 4 to 5 and some by-products can be detected and isolated, e.g. $Si(OEt)_4$ and products of the condensation reactions of triethoxysilane with the amine groups of substrates and products.[17,18] Many experiments have aimed at searching for catalysts which would increase both the yield and selectivity of the reaction. Under normal pressure, the maximum $\gamma + \beta$ yield is 80–85%,[19] which is reached in the presence of H_2PtCl_6-based catalysts[19,20] and particularly with activators.[21–25] Also the Pt(0) complex ($Pt(PPh_3)_4$) was used as an active catalyst which allowed workers to obtain aminopropylsilane with a yield of up to 70%.[6,26]

Like the hydrosilylation of allyl chloride, this process is also carried out under reflux of the reaction mixture. The temperature of the reaction mixture rises from 313 K to 393 K in air under normal pressure. The complex **I**, unlike $Pt(PPh_3)_4$, is stable to air but its activity is much higher than that of the most common catalysts used under similar conditions in the above process (Fig. 2).

Our examination confirmed the presence of the by-products formed in the following reaction Eqn [4].[17,18]

These by products (both isomers) underwent a reaction with ethanol giving additional portions of the γ-adduct (as well as β-adduct) (Eqn [5]):

Hydrosilylation of allyl methacrylate

The reaction proceeds according to Eqn [6]:

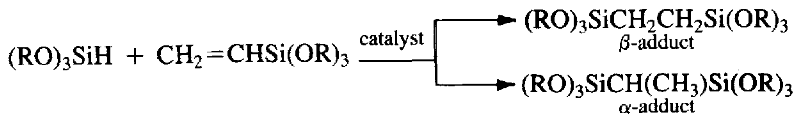
3-Methacryloxypropylsilanes are synthesized selectively in the above way, especially in the presence of platinum complexes based on H_2PtCl_6 precursors[27–34] as well as other Pt(IV)[35] or Pt(II) complexes.[35,36] The undesirable polymerization of the methacryloxy group, particularly in alkoxy-substituted silanes, during the addition reaction and distillation *in vacuo* can be eliminated by the introduction of inhibitors, e.g. diketones, ketoesters, etc.

The hydrosilylation of allyl methacrylate is a very exothermic reaction. In the presence of catalyst **I** the reaction proceeds smoothly with a similar or higher yield and selectivity as with other platinum complexes. Such a high activity of the Pt(0) complex allows us to use relatively low temperatures (323–343 K) for the reaction, reducing in this way the possibility of polymerization of the product as well as allowing the low concentration of the catalyst used. Selected results showing the effectiveness of this catalyst are presented in Table 5.

Hydrosilylation of vinyltriethoxysilane

The addition of trialkoxysilane to vinyltrialkoxysilane – a silane with an unsaturated C=C bond – proceeds according to Eqn [7]:

$$\underset{\text{(where X = Cl and EtO)}}{X_3SiH + CH_2{=}CHCH_2OCOC(CH_3){=}CH_2 \xrightarrow{\text{catalyst}} X_3SiCH_2CH_2CH_2OCOC(CH_3){=}CH_2} \quad [6]$$



[7]

Table 5 Yield of 3-methacryloxypropylsilanes (%) in the reaction of trichloro- and triethoxy-silane with allyl methacrylate catalysed by platinum complexes

Catalyst	Silane	Ratio [Pt]/[SiH]	Reaction time (h)	GC yield (%)
H_2PtCl_6(i-PrOH)	Cl_3SiH	10^{-4}	4	87
$PtCl_2(PPh_3)_2$	Cl_3SiH	10^{-4}	6.5	93
$Pt(PPh_3)_2(CH_2{=}CH_2)$	Cl_3SiH	10^{-4}	2	98
$Pt(PPh_3)_2(CH_2{=}CH_2)$	$(EtO)_3SiH$	10^{-4}	0.5	98
$Pt(PPh_3)_2(CH_2{=}CH_2)$	$(EtO)_3SiH$	10^{-5}	0.5	98

Exothermic reactions, air, $[\equiv SiH]:[\rangle C = C\langle] = 1:1$.

Table 6 Yield of 1,1- and 1,2-bis(triethoxysilyl)ethanes (α and β adducts, respectively) in the hydrosilylation of vinyltriethoxysilane by triethoxysilane catalysed by platinum complexes

	Yield of α and β adducts (%)			
Reaction conditions	353 K, 2 h		393 K, 6 h	
Catalyst	α	β	α	β
$Pt(PPh_3)_4$	0	0	6	69
$Pt(PPh_3)_2(CH_2{=}CH_2)$	3	89	7	79
$PtCl_2(PPh_3)_2$	2	22	8	78
H_2PtCl_6(i-PrOH)	8	78	8	82
H_2PtCl_6(⬡ = 0)	11	84	6	87

Air, glass ampoules, $[\equiv SiH]:[CH_2{=}CHSi\equiv]:[cat.] = 1:1:2 \times 10^{-4}$.

It is known that ruthenium complexes especially are very effective catalysts of this addition;[37,38] however, nickel and platinum precursors were also used, yielding satisfactory results.[37,39,40] There are only a few reports on platinum catalysts used in this system, e.g. H_2PtCl_6 (⬡ = 0).[37,39,41,42] The reported overall yields are not so high (up to 77%) and the selectivity is poor ($\beta : \alpha \approx 9$).[37,39] In Table 6 some experimental data for the reaction of vinyltriethoxysilane with triethoxysilane are presented. Complex **I** shows higher activity at 353 K, and a similar activity to those prepared from H_2PtCl_6 at higher reaction temperatures (e.g. 393 K), and is better than other Pt(0) and Pt(II) precursors, e.g. $Pt(PPh_3)_4$ or $PtCl_2(PPh_3)_2$.

CONCLUSION

All the hydrosilylation reactions examined proved the high catalytic effectiveness of complex **I**, $Pt(PPh_3)_2(CH_2{=}CH_2)$, presenting it as a new, versatile and very efficient catalyst of hydrosilylation for various alkenes as well as functionalized ones. Its characteristic features suggesting universal application [more positive than for the Speier catalyst or $Pt(PPh_3)_4$] are as follows:

- high selectivity and activity in the main direction (no redistribution products are observed);
- relative stability to air (compared with $Pt(PPh_3)_4$);
- possibility of recycling;
- relatively short induction period for the reaction catalysed.

According to the general scheme of Chalk and Harrod,[43] in the catalytic process of hydrosilylation in the presence of d^{10} complexes, e.g. Pt(0), initial complexation occurs via oxidative addition of hydrosilane to the Pt(0) complex, yielding a Pt(II) species. Activation of complex **I** by trisubstituted silanes is due to formation of a Pt(II)(silyl) hydride complex[10] followed by a coordination of olefin to give a catalytic process for the hydrosilylation.

Apparently, the three platinum catalysts below Pt(vinylsiloxane),[12] Pt(vinylsilane)[13] and Tsipis catalyst[44,45] also catalyse the hydrosilylation process via pathways close to those for complex **I**, i.e.

involving a Pt(0) → Pt(II) oxidative addition. Their use should allow us to account for the unexpectedly high activity of the system $Pt(PPh_3)_xL$ (where L = olefin, phosphine and other π-ligands and $x = 0-2$) in comparison with systems believed to involve a Pt(II) → Pt(IV) oxidative addition in the mechanism of the hydrosilylation reaction.

EXPERIMENTAL

Materials

(Alkyl, chloro)silanes as well as alkenes, allyl chloride and allylamine were commercial products distilled prior to use. Alkoxysilanes were prepared by solvolysis of the corresponding chlorosubstituted silanes according to standard procedures. Allyl methacrylate was obtained by transesterification of commercial methyl methacrylate.

Catalysts

$PtCl_2(PPh_3)_2$ was purchased from Ventron Chemicals, USA. $Pt(PPh_3)_4$[46] and $Pt(PPh_3)_2(CH_2{=}CH_2)$[47] were prepared according to the literature. The Speier catalyst[48] and H_2PtCl_6 in cyclohexanone[41] were synthesized from $H_2PtCl_6 \cdot 6H_2O$ solution.

Equipment and analytical measurements

Gas chromatography was carried out with a GCHF instrument using 2 m steel columns packed with 10% SE-30 on Gas Chrom Q (with a thermal conductivity detector).

Catalytic procedures

Most of the catalytic experiments were carried out in sealed glass ampoules under dry air (for details see the footnotes to Tables 1–6). In a typical run, a glass ampoule containing both substrates (1:1 ratio) and a catalyst was heated without a solvent at a given temperature for a given time. Products of hydrosilylation processes were identified by the GC technique. In the case of allyl chloride and allylamine, hydrosilylation reaction mixtures were heated under reflux.

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