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The reaction pathway from Speier's to Karstedt's hydrosilylation catalyst

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Abstract

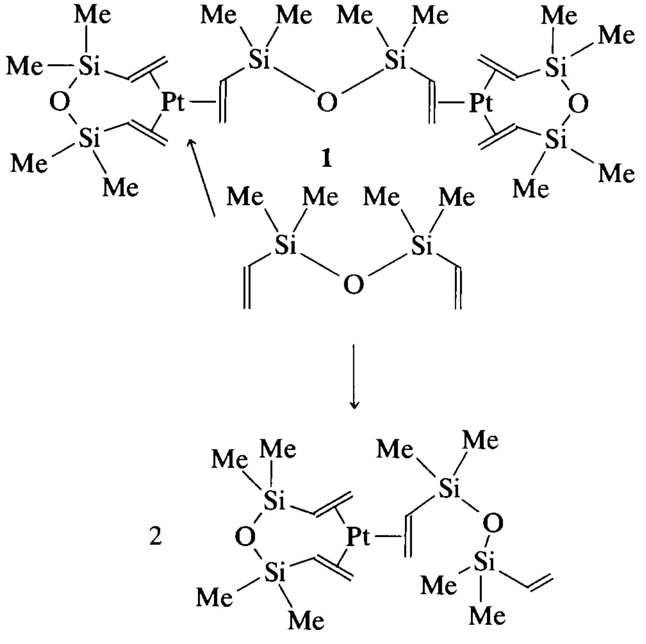
Multinuclear, variable temperature NMR spectroscopic experiments show that: (i) treatment of $[\{\overline{\text{Pt(LL)}}\}_2(\mu\text{-LL})]$, **1**, with an excess of $(CH_2{=}CHSiMe_2)_2O$ ($\equiv$ LL) yields $[\overline{\text{Pt(LL)}}(\text{LL})]$, **2**; (ii) treatment of **1** with $PhCH{=}CH_2$ gives $[\overline{\text{Pt(LL)}}(\eta^2\text{-}CH_2{=}CHPh)]$ **3**; and (iii) reaction of *cis*-$[Pt(\eta^2\text{-}CH_2{=}CHPh)Cl_2]$ with LL yields successively **1**, **2**, and **3**. The pathway in the case of (iii) involves initial chloride-vinyl exchange, followed by reductive elimination in which vinyl radicals and vinyl chloride may be involved.

Keywords: Silicon; Platinum; Hydrosilylation

An industrially useful modification of Speier's hydrosilylation catalyst $H_2[PtCl_6]\cdot xH_2O$ is obtained by treatment of the latter with the disiloxane $(CH_2{=}CHSiMe_2)_2O$ ($\equiv$ LL) [1]. We showed that from chloroplatinic acid and an excess of LL, after neutralisation with $Na[HCO_3]$ and filtration, there was obtained a solution **A** containing a Pt(0) species [2]. This was established by (i) $^{195}Pt\{^1H\}$ NMR spectroscopy, (ii) transformation of **A** into the X-ray-characterised $[\overline{\text{Pt(LL)}}\text{PBu}^t_3]$, and (iii) the identification of Pt-free volatiles from solution **A** as containing $Me_2RSiO(SiMe_2O)_xSiRMe_2$ ($x = 0$–4, but mainly $x = 0$; R = mainly $CH{=}CH_2$, some Et) and a trace of $CH_2{=}CHCl$. Subsequently we demonstrated that the Pt(0) component of solution **A** could also be formed from LL and $K_2[PtCl_4]$, $[\{Pt(CH_2{=}CH_2)Cl(\mu\text{-}Cl)\}_2]$, *cis*-$[Pt(\eta^2\text{-}CH_2{=}CHPh)_2Cl_2]$ or $[Pt(COD)_2]$; and the volatiles from Pt(II) or Pt(IV) chlorides also contained buta-1,3-diene and ethene [3]. Crystals obtained from solution **A** were shown crystallographically to have structure **1** [3].

We now report three series of multinuclear, variable temperature NMR spectroscopic experiments, the results of which we interpret as shown in Schemes 1–3, respectively.

In the first of these, Scheme 1, it is shown (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ and $^{195}Pt\{^1H\}$) that addition of the disiloxane LL to $[\{\overline{\text{Pt(LL)}}\}_2(\mu\text{-LL})]$ **1** in C_7D_8 at 298 K causes an equilibrium to be established between **1** and $[\overline{\text{Pt(LL)}}(\text{LL})]$ **2**, the concentration of the latter increasing with increasing concentration of LL. The broad nature of the signals of the methyl groups is believed to be due to the non-rigid structure of **2**, there being fast



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Scheme 1.

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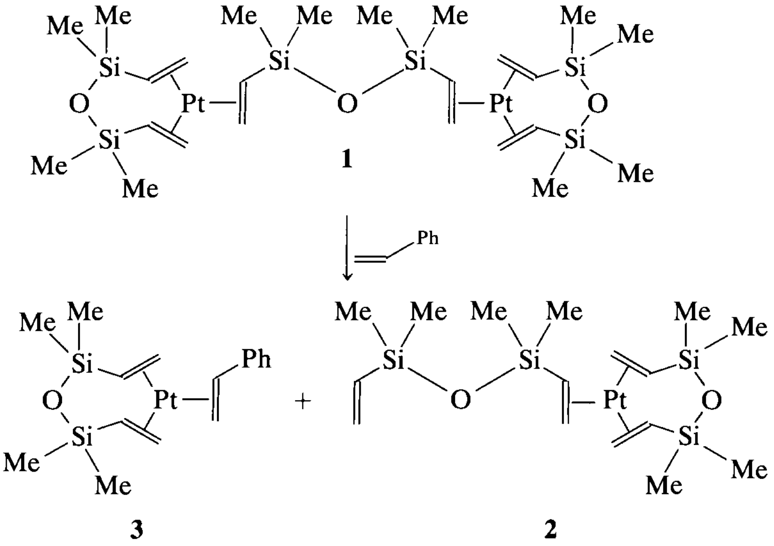
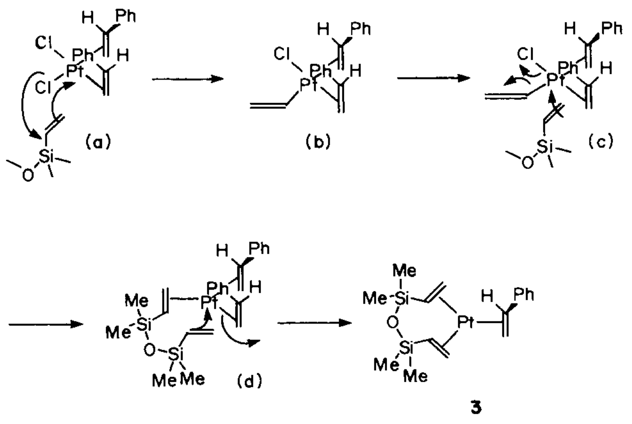


Scheme 2.

exchange between the pendant and chelating LL ligands. An unbound vinyl signal for **2** was observed at 218 K, and variable temperature and saturation transfer experiments showed that an exchange was observable between pendant and bound vinyl groups. The ^{195}Pt{^{1}H} signals at 303 K at δ −6141.1 and −6142.2 are assigned to two isomers of **1** (see also Refs. 2 and 3), and that at δ −6141.5 to that of **2**.

The nature of the equilibrium between **1** and an excess of styrene in C_7D_8 was shown to involve **2** and [$\overline{\mathrm{Pt(LL)}}$($\eta^2$-$CH_2$=CHPh)], **3**, Scheme 2. This was established by adding 1, 2 or 10 equivalents of PhCH=CH_2 to **1** and carrying out NMR spectroscopic studies involving ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{195}Pt{^{1}H} spectra, as well as saturation transfer, NOE and shift correlation. For **3**, four new signals for the methyl region, six for the vinyl region, two for ^{29}Si and one for ^{195}Pt (at δ −6019) were observed.

In order to to probe the pathway for the Pt(IV) $\xrightarrow{\mathrm{LL}}$ Pt(0) reduction, a model system was chosen which enabled a related reaction [between *cis*-dichlorobis(η^2-styrene)platinum(II) **4** and 7/2 equivalents of LL] to be monitored by variable temperature ^{195}Pt(^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy in 10% CD_2Cl_2 solution. A simplified proposed pathway is shown in Scheme 3. The salient feature is the proposal that the first step is the exchange between Pt(II) and Si of a $\overline{\mathrm{Cl}}$ with a $\overline{\mathrm{C}}$H=CH_2 ligand. The vinylplatinum(II) chloride [(b) in Scheme 3; though it was not identified] is then believed to undergo reductive elimination, in part by loss of CH_2=CHCl but mainly by a homolytic mechanism, the CH_2=$\dot{C}$H radical then affording CH_2=CH_2 or C_4H_6 by hydrogen atom abstraction or coupling, respectively.



Scheme 3.

The evidence for the proposal of Scheme 3 rests mainly on NMR spectroscopic identification successively of the Pt(II) complex (a), [$\overline{\mathrm{Pt(LL)}}$($\eta^2$-$CH_2$=CHPh)] **3**, **1**, and **2** as the temperature and concentration of LL is increased. Compound **4** is known to exist as three isomers, each with a characteristic ^{195}Pt{^{1}H} signal, differing in the relative conformation of the two styrene ligands [4]. At 233 K two of these signals at δ −3160.6 and −3282, were present in a ratio of ca. 3 : 1. At progressively higher temperatures, the former predominated; e.g., at 273 K, the signals (in 7 : 1 ratio) had shifted to δ −3145 and −3267; no Pt(0) signal was present. At 293 K only one broad Pt(II) signal at δ 3138 was present, but there were also two broad Pt(0) signals at δ −6136.5 and −6145, in a ratio of 9 : 2. After several hours, signals were observed at δ −6009 assigned to **3**, −6130 (unassigned), and −6139 (assigned to **1**), the last the least intense; addition of further PhCH=CH_2 caused the first signal to gain, and the last to lose, intensity.

We conclude, that the presence of the LL ligand at a Pt(0) centre favours three-coordination for the metal, which is then a 16-electron centre, in contrast to the 18-electron Pt in [Pt(COD)$_2$]. The lability of the bridging LL ligand in **1** probably accounts for its superior activity as a hydrosilylation catalyst, readily binding substrate alkene; and the resultant 16-electron complex still offers a vacant site for oxidative addition by a silane HSiX$_3$.

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