Addition of Anhydrous Hydrogen Chloride to Bis(ethynyl)bis(dimethylphenylphosphine)platinum(II). A Novel Sequence of Platinum(II) Promoted Addition–Elimination Reactions

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Summary *trans*-$[Pt(C{\equiv}CH)_2L_2]$ (I) reacts with anhydrous HCl (1 equiv.) to give *trans*-$[PtCl(C{\equiv}CH)L_2]$ (V) and acetylene by way of a sequence of reactions involving *trans*-$[Pt(C{\equiv}CH)(CCl{=}CH_2)L_2]$ (II), *trans*-$[Pt(CCl{=}CH_2)_2L_2]$ (III), and *trans*-$[PtCl(CCl{=}CH_2)L_2]$ (IV), where L = PMe_2Ph; the reaction sequence demonstrates that platinum(II) promotes both the rapid addition of HCl to a co-ordinated acetylide ligand and the ready elimination of HCl from the α-chlorovinyl ligand, $Pt\text{-}CCl{=}CH_2$.

Addition[†] of anhydrous HCl (1 equiv.) to a solution of *trans*-$[Pt(C{\equiv}CH)_2L_2]$ (I) in $CDCl_3$ or CD_2Cl_2 caused an apparently instantaneous reaction, even at −60 °C, and gave a mixture of (I), *trans*-$[Pt(C{\equiv}CH)(CCl{=}CH_2)L_2]$ (II),

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[†] Reactions were carried out using standard vacuum line techniques and followed by ^1H n.m.r. spectroscopy. Satisfactory analytical data were obtained for all compounds except (II), which we have not isolated free from (I) and (III). Pertinent characterization data for compound (I)—(V) are given below. All ^1H n.m.r. data were recorded at 60 MHz at 30 °C in CD_2Cl_2 with Me_4Si as internal reference. (I) δ 2·05 ($^3J_{Pt-H}$ 33·0, $^2J + {}^4J_{P-H}$ 7·8 Hz, PMe) and 2·13 ($^3J_{Pt-H}$ 45, $^4J_{P-H}$ 2·3 Hz, $C{\equiv}CH$), $\nu(C{\equiv}C\text{–}H)$ 3268 and 1968 cm^{-1}, m.p. 173 °C; (II) 5·92 ($^3J_{Pt-H}$ 68, $^4J_{P-H}$ 1·8 Hz, *trans*-$Pt\text{–}C{=}CH$) and 4·82 ($^3J_{Pt-H}$ 25·5, $^4J_{P-H}$ 1·6 Hz, *cis*-$Pt\text{-}C{=}CH$), other resonances and couplings are similar to those for (I), $\nu(C{\equiv}CH)$ 3288 and 1973 cm^{-1}; (III) J_{H-H} ($Pt\text{–}C{=}CH_2$) 0·6 Hz (*gem* coupling), other resonances and couplings are similar to those for (I) and for (II), $\nu(ClC{=}CH_2)$ 1565 cm^{-1}, m.p. 130 °C; (IV) δ 5·93 ($^3J_{Pt-H}$ 114, $^4J_{P-H}$ 1·5 Hz, *trans*-$Pt\text{–}C{=}CH$) and 4·92 ($^3J_{Pt-H}$ 43·2, $^4J_{P-H}$ 1·7 Hz, *cis*-$Pt\text{–}C{=}CH$), other resonances and couplings similar to those for (III), $\nu(ClC{=}CH_2)$ 1630 cm^{-1}, m.p. 96 °C; (V) δ 2·12 ($^3J_{Pt-H}$ 71·6, $^4J_{P-H}$ 2·3 Hz, $C{\equiv}CH$), P*Me* resonances and couplings similar to those for (I), $\nu(C{\equiv}C\text{-}H)$ 3278 and 1987 cm^{-1}, m.p. 149 °C.

and *trans*-$[Pt(CCl{=}CH_2)_2L_2]$ (III) in the ratio *ca.* 1:2:1 respectively (L = PMe_2Ph throughout). After 12 h at 25 °C further reaction had occurred to give a 1:1 mixture of (I) and *trans*-$[PtCl(CCl{=}CH_2)L_2]$ (IV). Analysis of the volatile organic products showed that at $t = 0$ (immediately after adding HCl), only a trace of acetylene had been liberated and that at $t = 12$ h [1:1 mixture of (I) and (IV)], acetylene was present in almost 50% yield based on added HCl. Significantly, only a trace of vinyl chloride was detected at $t = 12$ h and no *trans*-$[PtCl(C{\equiv}CH)L_2]$ (V) was observed in either the ^1H n.m.r. spectra recorded during the course of the reaction or in the i.r. spectrum of $t = 0$ and $t = 12$ h platinum-containing solids. The initial reaction between (I) and HCl (1 equiv.) in $CDCl_3$ and CD_2Cl_2 can be represented as shown in equation (1). It is noteworthy that

$$4(I) + 4HCl \rightarrow (I) + 2(II) + (III) \rightarrow 2(I) + 2(IV) + 2HC{\equiv}CH \quad (1)$$

(II) exists in equilibrium with (I) and (III): (I) + (III) $\rightleftharpoons$ 2(II); *K ca.* 1.

When equimolar quantities of (I) and *trans*-$[Pt(CCl{=}CD_2)_2L_2]$, $[^2H_4]$-(III),‡ were dissolved in CD_2Cl_2, the ^1H n.m.r. spectrum showed that the formation of the 1:2:1 mixture of (I), (II), and (III), which occurred in <2 min at 25 °C, was accompanied by complete H/D scrambling of vinylic protons. The i.r. spectrum showed the presence of both Pt–C≡CH and Pt–C≡CD groups in (I) and (II).§

Addition of HCl (1 equiv.) to (I) in C_6D_6 and $C_5D_5CD_3$ gave initially a 1:1 mixture of (I) and (III) which during *ca.* 24 h at 25 °C gave a mixture of (I), (II), and (III) in the ratio *ca.* 1:2:1 respectively. Further reaction to give (IV) and acetylene was exceedingly slow, requiring *ca.* 6 weeks to reach completion at 25 °C.

Addition of anhydrous HCl (2 equiv.) to (I) in $CDCl_3$, CD_2Cl_2, and C_6D_6 led to almost quantitative formation of (III) which melts at 130 °C with effervescence to yield (IV) and acetylene. A mixture of (III) and $[^2H_4]$-(III) co-crystallized from benzene and melted to give predominantly HC≡CD.

Compound (III) is unstable in $CDCl_3$ and CD_2Cl_2 and decomposes to give (IV) and HC≡CH during 12 h at 25 °C. This reaction is much slower in $[^2H_8]$-*p*-dioxan (*ca.* 11 days, 25 °C) and C_6D_6 (several weeks, 25 °C).

Addition of HCl (1 equiv.) to (III) in CD_2Cl_2 and C_6D_6 gives (IV) and vinyl chloride quantitatively. This, however, was a relatively slow reaction in $C_5D_5CD_3$. Addition of HCl (1 equiv.) to $[^2H_4]$-(III) in $C_5D_5CD_3$ showed that a reaction leading to the H/D exchange of vinyl protons occurred much faster than elimination of vinyl chloride. Rather interestingly, (IV) does not react with anhydrous HCl in $CDCl_3$, CD_2Cl_2, or C_6D_6 to liberate vinyl chloride.

Compound (III) reacts with anhydrous NH_3 and Me_3N (1 equiv.) in CD_2Cl_2 to give an immediate precipitate of the amine hydrochloride and the *ca.* 1:2:1 mixture of (I), (II), and (III). This reaction also occurred in C_6D_6 but at a markedly slower rate.

The 1:1 mixture of (I) and (IV) formed in the reaction between (I) and HCl (1 equiv.) (equation 1) underwent further reaction in CD_2Cl_2 and $CDCl_3$ to give (V) and acetylene. This reaction arises because (IV) is itself labile to the reversible elimination of HCl. Formation of (V) from the reaction between (I) and (IV) is, however, exceedingly slow ($t_{\frac{1}{2}}$ *ca.* 30 days, 44 °C, $CDCl_3$) and (V) is best prepared by the circuitous route of dissolving (IV) in MeOH saturated with NH_3. The overall reaction between (I) and HCl (1 equiv.) to give (V) and acetylene *via* (II), (III), and (IV) is shown in the Scheme. This may be compared with previous observations of the reactions between platinum(II) acetylides and HCl which gave compounds of the types $[L_2Pt(C{\equiv}CR)Cl]$,[1,2] $[L_2Pt(CCl{=}CHR)_2]$[3], and $[L_2PtCl(CCl{=}CHR)]$[1,2] depending on the nature of the group R. However, the lability of the α-chlorovinyl ligand toward ready elimination of HCl has not previously been noted. This may also be dependent on the nature of R as we find that $[L_2Pt(CCl{=}CHCF_3)_2]$ does not react with $AgPF_6$ in methanol to give AgCl.

$$4(I) + 4HCl \rightarrow (I) + 2(II) + (III)$$
$$2(II) \rightleftharpoons (I) + (III); \ K \ ca. \ 1$$
$$(III) \rightarrow (IV) + HC{\equiv}CH$$
$$(I) + (IV) \rightarrow (V) + HC{\equiv}CH$$
$$4(I) + 4HCl \rightarrow (I) + 2(II) + (III) \rightarrow 2(I) + 2(IV) + 2HC{\equiv}CH \rightarrow 4(V) + 4HC{\equiv}CH$$

SCHEME

Since acetylene and HCl do not react under the above conditions[4] and vinyl chloride is similarly stable with respect to the formation of acetylene and HCl, the reaction between (I) and HCl demonstrates that platinum(II) promotes both the rapid addition of HCl to the σ-co-ordinated acetylide and the ready elimination of HCl from the α-chlorovinyl ligand $Pt{-}CCl{=}CH_2$.

Both elimination of HCl from (II), (III), and (IV) and the decomposition of (III) to (IV) and acetylene, occur in the following order: $CD_2Cl_2 \sim CDCl_3 >> C_6D_6$.

Further studies on the mechanism of these reactions are in progress. Preliminary results from kinetic and labelling experiments are consistent with mechanisms involving platinum vinyl carbonium ions, $Pt{-}C^+{=}CH_2$.

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‡ Prepared from the reaction of DCl (2 equiv) with $[^2H_2]$-(I); the latter was prepared by dissolving (I) in MeOD in the presence of a trace of OD^-, ν(C≡C–D) 1855 and 2510 cm^{-1}.

§ The reaction was quenched by removing solvent under reduced pressure as soon as a 1:2:1 distribution was attained (< 2 min). Characteristic ν(–C≡C–D) frequencies were observed at 1855 and 2510 cm^{-1}.

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