

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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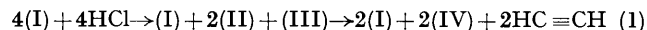
Summary *trans*-[Pt(C≡CH)₂L₂] (I) reacts with anhydrous HCl (1 equiv.) to give *trans*-[PtCl(C≡CH)L₂] (V) and acetylene by way of a sequence of reactions involving *trans*-[Pt(C≡CH)(C≡CH)L₂] (II), *trans*-[Pt(CCl=CH)₂L₂] (III), and *trans*-[PtCl(CCl=CH₂)L₂] (IV), where L = PMe₂Ph; the reaction sequence 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-C≡CH₂.

ADDITION† of anhydrous HCl (1 equiv.) to a solution of *trans*-[Pt(C≡CH)₂L₂] (I) in CDCl₃ or CD₂Cl₂ caused an apparently instantaneous reaction, even at -60 °C, and gave a mixture of (I), *trans*-[Pt(C≡CH)(C≡CH)L₂] (II),

† 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 CD₂Cl₂ with Me₄Si 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} 4.5, ⁴J_{P-H} 2.3 Hz, C≡CH), ν(C≡C-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-C=CH) and 4.82 (³J_{Pt-H} 25.5, ⁴J_{P-H} 1.6 Hz, *cis*-Pt-C=CH), other resonances and couplings are similar to those for (I), ν(C≡CH) 3288 and 1973 cm⁻¹; (III) J_{H-H} (Pt-C=CH₂) 0.6 Hz (*gem* coupling), other resonances and couplings are similar to those for (I) and for (II), ν(C=C-H) 1565 cm⁻¹, m.p. 130 °C; (IV) δ 5.93 (³J_{Pt-H} 114, ⁴J_{P-H} 1.5 Hz, *trans*-Pt-C=CH) and 4.92 (³J_{Pt-H} 43.2, ⁴J_{P-H} 1.7 Hz, *cis*-Pt-C=CH), other resonances and couplings similar to those for (III), ν(C=C-H) 1630 cm⁻¹, m.p. 96 °C; (V) δ 2.12 (³J_{Pt-H} 71.6, ⁴J_{P-H} 2.3 Hz, C≡CH), PMe resonances and couplings similar to those for (I), ν(C≡C-H) 3278 and 1987 cm⁻¹, m.p. 149 °C.

and *trans*-[Pt(CCl=CH₂)₂L₂] (III) in the ratio *ca.* 1:2:1 respectively (L = PMe₂Ph throughout). After 12 h at 25 °C further reaction had occurred to give a 1:1 mixture of (I) and *trans*-[PtCl(CCl=CH₂)L₂] (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≡CH)L₂] (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 CDCl₃ and CD₂Cl₂ can be represented as shown in equation (1). It is noteworthy that



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

When equimolar quantities of (I) and *trans*-[Pt(CCl=CD₂)₂L₂], [²H₄]- (III),[‡] were dissolved in CD₂Cl₂, 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 C₆D₆ and C₅D₅CD₃ 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 CDCl₃, CD₂Cl₂, and C₆D₆ led to almost quantitative formation of (III) which melts at 130 °C with effervescence to yield (IV) and acetylene. A mixture of (III) and [²H₄]- (III) co-crystallized from benzene and melted to give predominantly HC≡CD.

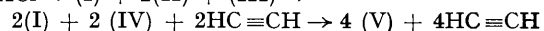
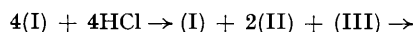
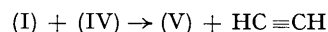
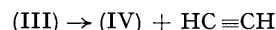
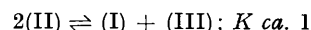
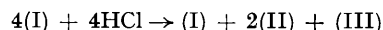
Compound (III) is unstable in CDCl₃ and CD₂Cl₂ and decomposes to give (IV) and HC≡CH during 12 h at 25 °C. This reaction is much slower in [²H₈]-*p*-dioxan (*ca.* 11 days, 25 °C) and C₆D₆ (several weeks, 25 °C).

Addition of HCl (1 equiv.) to (III) in CD₂Cl₂ and C₆D₆ gives (IV) and vinyl chloride quantitatively. This, however, was a relatively slow reaction in C₅D₅CD₃. Addition of HCl (1 equiv.) to [²H₄]- (III) in C₅D₅CD₃ 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 CDCl₃, CD₂Cl₂, or C₆D₆ to liberate vinyl chloride.

Compound (III) reacts with anhydrous NH₃ and Me₃N (1 equiv.) in CD₂Cl₂ 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 C₆D₆ 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 CD₂Cl₂ and CDCl₃ 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*_{1/2} *ca.* 30 days, 44 °C, CDCl₃) and (V) is best prepared by the circuitous route of dissolving (IV) in MeOH saturated with NH₃. The overall reaction between (I) and HCl (1



SCHEME

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 [L₂Pt(C≡CR)Cl]^{1,2}, [L₂Pt(CCl=CHR)₂]³, and [L₂PtCl(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 [L₂Pt(CCl=CHCF₃)₂] does not react with AgPF₆ in methanol to give AgCl.

Since acetylene and HCl do not react under the above conditions⁴ 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=CH₂.

Both elimination of HCl from (II), (III), and (IV) and the decomposition of (III) to (IV) and acetylene, occur in the following order: CD₂Cl₂ ~ CDCl₃ >> C₆D₆.

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⁺=CH₂.

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[‡] Prepared from the reaction of DCl (2 equiv) with [²H₂]- (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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