Alcoholysis Reactions of Chloroplatinum(II) Chlorovinyl Compounds

By ROBERT A. BELL and MALCOLM H. CHISHOLM*

(*Frick Chemical Laboratories, Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)

Summary The chloroplatinum(II) chlorovinyl compounds *trans*-$PtCl[CCl{=}C(H)R^1](PMe_2Ph)_2$, ($R^1$ = Me and Ph), react with alcohols R^2OH to give alkoxycarbene complexes *trans*-$\{PtCl[C(OR^2)CH_2R^1](PMe_2Ph)_2\}^+Cl^-$, ($R^2$ = Me, Et, and Pr^n), which may be isolated as stable hexafluorophosphate salts by the addition of $AgPF_6$.

SIMPLE vinyl halides are highly unreactive in solvolytic processes:[1] the presence of silver salts, such as silver nitrate, does not facilitate cleavage of the carbon–halogen bond. We report here the remarkable lability of the carbon-halogen bond in the compounds *trans*-$PtCl[CCl = C(H)R](PMe_2Ph)_2$ where R = Me and Ph.

The addition of HCl to *trans*-$PtCl(C{\equiv}CR)(PMe_2Ph)_2$ where R = Me and Ph, leads[2] to the formation of the chlorovinyl compounds *trans*-$PtCl[CCl = C(H)R](PMe_2Ph)_2$. The ^1H n.m.r. spectrum of the methylvinyl compound (R = Me) (**1**) in CD_2Cl_2, $CDCl_3$, and benzene shows[2] the presence of (i) *trans*-PMe_2Ph ligands and (ii) both *cis*- and *trans*-$PtCCl{=}C(H)Me$ isomers. However, we now find that (**1**) dissolves in methanol with apparently immediate and quantitative formation of *trans*-$\{PtCl[C(OMe)Et](PMe_2Ph)_2\}^+Cl^-$. This is clearly evident from the ^1H n.m.r. spectrum of (**1**) in methanol. The phosphine methyl proton resonances appear as overlapping sets of 1:2:1 triplets indicating the presence of *trans*-PMe_2Ph ligands and the absence of a plane of symmetry about the $ClPtP_2$ unit. The latter results from restricted rotation about the Pt–carbene bond. The alkoxy-carbene ligand is clearly indicated by the following: Me, 1:4:1 triplet, δ 4·80 (rel. to Me_4Si), J_{Pt-H} 9 Hz; CH_2Me, obscured by the PMe_2Ph resonances; CH_2Me, 1:2:1 triplet, δ 0·60, J_{HH} 7 Hz. Although *trans*-$\{PtCl[C(OMe)Et](PMe_2Ph)_2\}^+Cl^-$ is apparently formed quantitatively on dissolving (1) in methanol, it slowly reacts to give *trans*-$PtCl(COEt)(PMe_2Ph)_2$ and MeCl. This substantiates a previous suggestion.[2]

The generality of the above alcoholysis reaction is indicated by reaction (1) which affords a new route[3] to stable alkoxy carbene complexes.

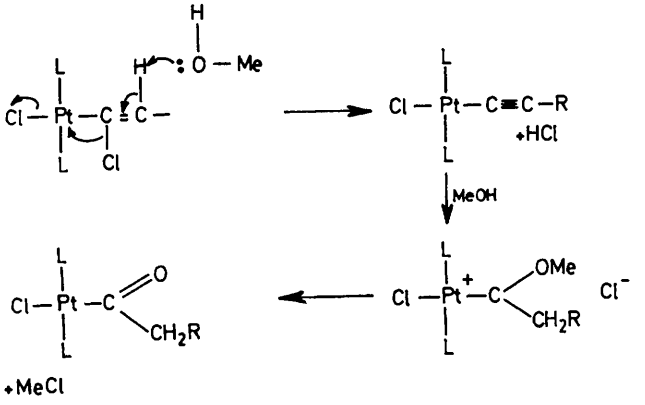
$$\textit{trans}\text{-PtCl[CCl} = \text{C(H)R}^1](\text{PMe}_2\text{Ph})_2 + \text{AgPF}_6 \xrightarrow{\text{R}^2\text{OH}} \textit{trans}\text{-PtCl[C(OR}^2)\text{CH}_2\text{R}^1]\,(\text{PMe}_2\text{Ph})_2]^+\text{PF}_6^- + \text{AgCl} \quad (1)$$

where R^1 = Me and Ph and R^2 = Me, Et and Pr^n.

We suggest that these reactions proceed *via* the mechanism shown in the Scheme. Consistent with this proposal are the following observations: (i) Alcoholysis reactions of $PtX[CCl = C(H)R](PMe_2Ph)_2$ only occur when the Pt–X bond is labile towards Pt^+X^- heterolysis, *e.g.* X = Cl, Br, and I. (ii) Reaction of $PtBr[CCl{=}C(H)Me](PMe_2Ph)_2$ with $AgPF_6$ in methanol gives only the chloroplatinum carbene complex *trans*-$\{PtCl[C(OMe)Et](PMe_2Ph)_2\}^+PF_6^-$. (Analysis showed <0·1% Br). (iii) Reaction in CH_3OD shows that the vinylic hydrogen is lost to the solvent [reaction (2)]. This is clearly evident from the ^1H n.m.r. spectrum: the $CD_2\mathit{Me}$ resonance appears as a singlet. (iv) (**1**) dissolves in methanol saturated with anhydrous NH_3 to give *trans*-$PtCl(C{\equiv}CMe(PMe_2Ph)_2$ and NH_4Cl; no formation of *trans*-$\{PtCl[C(NH_2)Et](PMe_2Ph)_2\}^+Cl^-$ is observed. (v) (**1**) does not react with anhydrous NH_3 in benzene, *cf.* (iv) above.

$$\text{PtCl[CCl} = \text{C(H)Me](PMe}_2\text{Ph)}_2 \xrightarrow{\text{CH}_3\text{OD}} \textit{trans}\{\text{PtCl[C(OMe)CD}_2\text{Me](PMe}_2\text{Ph)}_3\}^+\text{Cl}^- \quad (2)$$

The observations (i)—(v) above demonstrate the importance of Pt–Cl heterolysis and that H^+ is abstracted by the solvent. They do not, however, allow a distinction between a concerted or a stepwise elimination of the elements of HCl.



SCHEME

Although the reactions reported here are without precedent we note that the recently reported[4] formation of dicyanovinylidene complexes presumably proceed *via* migration of a vinylic chloride to the metal.

We thank Mathey-Bishop, Inc. for a loan of platinum, and the donors of the Petroleum Research Fund administered by the American Chemical Society and the National Science Foundation for financial support.

(*Received*, 29*th July* 1974; *Com.* 958.)

---

[1] M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209.

[2] M. H. Chisholm and D. A. Couch, *J.C.S. Chem. Comm.*, 1974, 42.

[3] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487; D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; E. O. Fischer, *Pure Appl. Chem.*, 1972, **30**, 353.

[4] R. B. King and M. S. Saran, *J.C.S. Chem. Comm.*, 1972, 1053; *J. Amer. Chem. Soc.*, 1973, **95**, 1817; R. M. Kirchner, J. A. Ibers, M. S. Saran, and R. B. King, *ibid.*, 1973, **95**, 5776.