Reactions of Propynylplatinum(II) Compounds

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Summary The alkynylplatinum(II) compounds *trans*-$\mathrm{Pt(C{\equiv}CR)_2L_2}$ and *trans*-$\mathrm{PtCl(C{\equiv}CR)L_2}$ ($\mathrm{R{=}Me}$ or $\mathrm{CF_3}$; $\mathrm{L{=}PMe_2Ph}$) show interesting chemistry based on reaction at either the organic or inorganic site of unsaturation; a new synthesis of alkoxy-carbene ligands and evidence for platinum-stabilized carbonium ion intermediates are reported.

THE reactions of protic acids, HX, with *trans*-$\mathrm{Pt(C{\equiv}CR)_2L_2}$ and *trans*-$\mathrm{PtCl(C{\equiv}CR)L_2}$ ($\mathrm{R = Me}$ or $\mathrm{CF_3}$; $\mathrm{L = PMe_2Ph}$) depends on X, R, and the solvent (see Scheme 1). Thus, *e.g.*, anhydrous HCl (1 mol. equiv.) reacts almost quantitatively with *trans*-$\mathrm{PtCl(C{\equiv}CMe)L_2}$ to give: (i) *cis*- and *trans*-$\mathrm{PtCl_2L_2}$ in $\mathrm{CH_2Cl_2}$; (*ii*) *trans*-$\mathrm{PtCl[CCl{=}C(H)Me]L_2}$ in tetrahydrofuran (THF); and (iii) *trans*-$\mathrm{PtCl(COEt)L_2}$ in methanol. *cis–trans*-Addition to the triple bond {leading to $\mathrm{PtCl[CCl{=}C(H)Me]L_2}$} occurs in the ratio 3:2. This assignment is based on ^{1}H n.m.r. data.† Similar reactions

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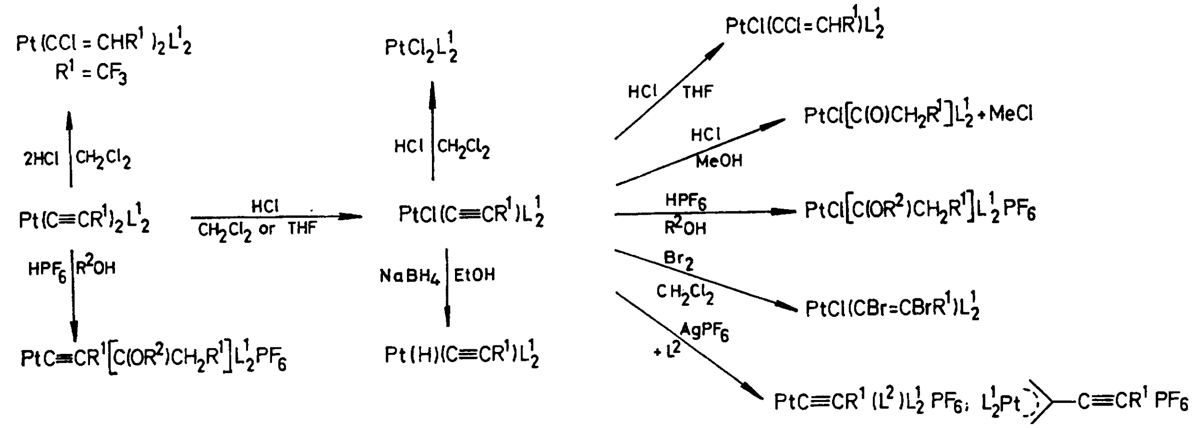
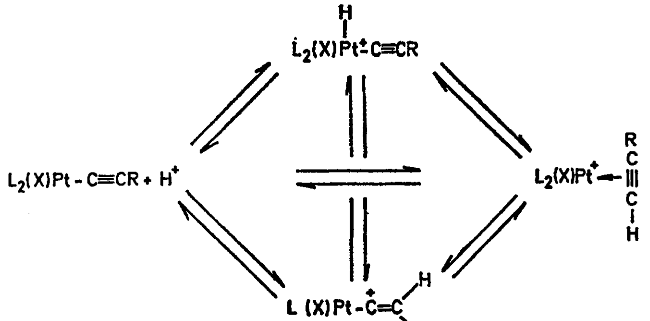
† $\mathrm{CD_2Cl_2}$ solution, $\mathrm{Me_4Si}$ internal reference: for $\mathrm{PtCCl{=}C(Me)H}$ δ (=CH) for Cl, Me *trans*, 6·02; $^3J_{\mathrm{HH}}$ 7·4, $^4J_{\mathrm{PH}}$ 2·0, $^3J_{\mathrm{PtH}}$ 90·0 Hz; δ (=CH) for Cl, Me *cis*, 5·11 $^3J_{\mathrm{HH}}$ 6·8, $^4J_{\mathrm{PH}}$ 1·6, $^3J_{\mathrm{PtH}}$ 45·0 Hz.



R^1 = Me; R^2 = Me, Et, Pr^n, Pr^i. L^1 = PMe_2Ph; L^2 = 2-oxacyclopentylidene, CO, py, MeCN, and allene (*cf.* ref. 4).

SCHEME 1. Some reactions of propynylplatinum(II) compounds. Satisfactory analytical data were obtained for all complexes.

occur with CF_3CO_2H; in CH_2Cl_2, addition to the acetylenic triple bond and propyne elimination are competing reactions, whilst in MeOH, alkoxy-carbene formation, *trans*-$[PtCl\{C(OMe)Et\}L_2]^+$ $[O_2CCF_3]^-$, followed by slow conversion into the propionyl platinum complex *trans*-$PtCl(COEt)L_2$, with elimination of CF_3CO_2Me, is observed.‡ Protic acids HX, where X^- is non-nucleophilic and hence inert to this type of alkylation, *e.g.* PF_6^-, react with *trans*-$Pt(C{\equiv}CMe)_2L_2$ and *trans*-$PtCl(C{\equiv}CMe)L_2$ in alcohols ROH to yield stable alkoxycarbene complexes, *trans*-$[PtC{\equiv}CMe\{C(OR)Et\}L_2]^+$ X^- and *trans*-$[PtCl\{C(OR)Et\}L_2]^+$ X^-, respectively (R = Me, Et, Pr^n, and Pr^i). Addition of LiCl (1 mol. equiv.) to an acetone solution of *trans*-$[PtCl\{C(OMe)Et\}L_2]^+$ PF_6^- gives *trans*-$PtCl(COEt)L_2$, MeCl, and $LiPF_6$. Thus we believe that in the reaction of *trans*-$PtCl(C{\equiv}CMe)L_2$ with HCl in MeOH the propionyl complex *trans*-$PtCl(COEt)L_2$ is formed *via* an unstable carbene complex, *trans*-$[PtCl\{C(OMe)Et\}L_2]^+$ Cl^-, which readily eliminates MeCl. A catalytic amount of HPF_6 reacts with *trans*-$PtCl(C{\equiv}CMe)L_2$ in water to yield *trans*-$PtCl(COEt)L_2$, presumably *via* an unstable hydroxy-carbene complex,[1] *trans*-$[PtCl\{C(OH)Et\}L_2]^+$ PF_6^-, which is readily deprotonated by the solvent. In contrast to the above reactions, the trifluoropropynyl complex *trans*-$Pt(C{\equiv}CCF_3)_2L_2$ reacts with anhydrous HCl in CH_2Cl_2 to yield only vinylic products arising from addition to the triple bond;[2] we observe no reaction with 1 mol. equiv. of either HCl or HPF_6 in MeOH.



SCHEME 2

Alcoholic protonation of a metal-alkynyl complex offers a new and probably quite general route to alkoxy-carbene complexes.[3] Since protonation–deprotonation may occur rapidly in the above reactions (especially in solvents such as THF and MeOH), the initial or preferential site of protonation (*i.e.* platinum or the acetylenic triple bond) is uncertain. Thus for alkoxy-carbene formation, any of the reactions shown in Scheme 2 leading to the platinum-stabilized vinyl cation $PtC^+{=}C(H)Me$ could be operative. These findings complement earlier work[4] which showed that terminal acetylenes co-ordinated to organoplatinum cations gave alkoxy-carbene ligands in MeOH and EtOH and acetylides in other solvents such as THF.

$PtCl(C{\equiv}Me)L_2$ very rapidly reacts with 1 mol. equiv. each of Cl_2, Br_2, and I_2 in dichloromethane at room temperature. The mode of reaction differs for each halogen: I_2 gives the oxidative-addition product *trans*-$PtCl(I)_2(C{\equiv}CMe)L_2$; Br_2 reacts exclusively by addition to the triple bond giving *trans*-$PtCl[CBr{=}C(Br)Me]L$;§ whilst for Cl_2 the reaction is more complex and leads to a mixture of products which include some unchanged $PtCl(C{\equiv}CMe)L_2$.

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‡ The reaction *tran*-$[PtCl\{C(OMe)Et\}L_2]^+[CF_3CO_2]^- \rightarrow$ *trans*-$PtCl(COEt)L_2$ + CF_3CO_2Me in dichloromethane is readily followed by n.m.r. spectroscopy.

§ We observe only one vinylic isomer which we believe corresponds to *trans*-addition to the propynyl ligand: for PtCBr = C(Br)Me, δ(Me) for Br, Br *trans* 2·07; J_{PH} 2·4 Hz, J_{PtH} 15 Hz.

[1] M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc.* (*A*), 1971, 794; J. R. Moss, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 975.

[2] A similar observation for L = PEt_3 has been reported: M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 356.

[3] (a) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487; (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; *Chem. Soc. Rev.*, 1973, **2**, 99.

[4] M. H. Chisholm and H. C. Clark, *Accounts Chem. Res.*, 1973, **6**, 202.