Nucleophilicity of Zerovalent Platinum Acetylene Complexes

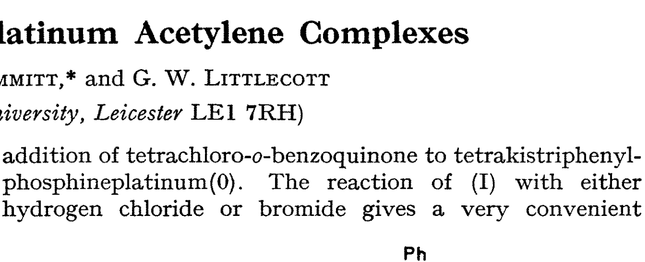
By D. M. BARLEX, R. D. W. KEMMITT,* and G. W. LITTLECOTT

(*Chemistry Department, The University, Leicester* LE1 7RH)

Summary Tetrachloro-*o*-benzoquinone undergoes a novel oxidative-elimination reaction with $Pt(PhC{\equiv}CPh)(PPh_3)_2$ to give the platinum(II) diphenylacetylene complex, $Pt(O_2C_6Cl_4)(PhC{\equiv}CPh)(PPh_3)$: mercuric halides add to $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$ to give vinyl complexes, *cis*-$PtCl[CF_3C{=}C(HgCl)CF_3](PMePh_2)_2$, with retention of configuration about the double bond and platinum.

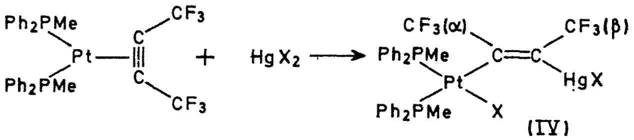
ALTHOUGH fluoro-olefins or -acetylenes are not very susceptible to electrophilic attack, co-ordination to rhodium(I)[1] or platinum(0)[2] greatly enhances their reactivity towards protonic acids. All these reactions presumably proceed *via* an initial oxidative addition of the acid to the metal. Thus, in the reactions with zerovalent platinum acetylene complexes, a platinum(II) acetylene complex is probably involved as an intermediate, although hitherto no evidence for this type of oxidative reaction has been reported. We now report that addition of tetrachloro-*o*-benzoquinone to $Pt(PhC{\equiv}CPh)(PPh_3)_2$ does afford a platinum(II) acetylene complex (I) in a novel oxidative-elimination reaction.

Addition of tetrachloro-*o*-benzoquinone in benzene to a benzene solution of $Pt(PhC{\equiv}CPh)(PPh_3)_2$ results in the immediate precipitation of a pale yellow solid (I). The i.r. spectrum of (I) exhibits bands typical of the co-ordinated quinone (1259, 978, and 804 cm^{-1}) and in addition a weak band at 1961 cm^{-1} is observed typical of an acetylene co-ordinated to platinum(II). Further evidence for the structure of (I) is provided by its reaction with triphenylphosphine to give (II) which is also readily obtained by addition of tetrachloro-*o*-benzoquinone to tetrakistriphenylphosphineplatinum(0). The reaction of (I) with either hydrogen chloride or bromide gives a very convenient synthesis of the platinum(II) diphenylacetylene complexes (III). The i.r. spectrum (Nujol) of the chloride complex exhibits weak bands at 1965 and 1990 cm^{-1} due to $\nu(C{\equiv}C)$ and two platinum–chlorine stretching frequencies at 332 and 298 cm^{-1} suggesting a *cis*-configuration for the complex. This reaction clearly illustrates how the oxidation state of the central metal can affect the reactivity of co-ordinated diphenylacetylene, since $Pt(PhC{\equiv}CPh)(PPh_3)_2$ reacts with acids to give a vinyl complex.[2–4]



The spontaneous addition of tetrachloro-*o*-benzoquinone to platinum(0) complexes should be contrasted with the recent photoinduced oxidative addition of 9,10-phenanthrenequinone and 1,2-naphthoquinone to *trans*-$IrCl(CO)(PPh_3)_2$.[5] In other studies we have shown that the more reactive tetrachloro-*o*-benzoquinone adds spontaneously to the complexes *trans*-$MCl(CO)(PPh_3)_2$, (M = Rh or Ir).

Further indication of the nucleophilicity of zerovalent platinum acetylene complexes can be judged by the reactions of mercury(II) halides with $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$. Thus, on heating an ethanolic solution of $Pt(CF_3C{=}CCF_3)(PMePh_2)_2$ under reflux with mercury(II) chloride or bromide the complexes (IV) are readily isolated. The i.r. spectrum of the chloride complex exhibits a C=C stretching frequency at 1578 cm^{-1} and metal–chlorine stretching frequencies at 348 and 310 cm^{-1}. The ^{19}F n.m.r. spectrum (relative to benzotrifluoride) shows a quintet at −10·54 p.p.m. assigned to F_α and a quartet at −8·58 p.p.m. assigned to F_β. The quintet arises since in addition to F–F coupling the *trans*-phosphine ligand also couples with the signal such that $J(F\text{–}F) \approx J(P\text{–}F) = 11{\cdot}6$ Hz. This signal is further split into two smaller quintets due to coupling with ^{195}Pt, $J(Pt\text{–}F) = 86{\cdot}2$ Hz. The quartet arises since F_β complexes with F_α, $J(F\text{–}F) = 11{\cdot}6$ Hz. The magnitude of $J(F\text{–}F)$ clearly implies a *cis*-configuration about the double bond. Since F_α only couples with one phosphine ligand it is also apparent that the platinum complex has a *cis*-configuration. This is confirmed by the ^1H n.m.r. since the methyl group on the phosphine ligands appears as a doublet. The ^1H and ^{19}F n.m.r. spectra of the bromide complex establish a similar structure. The presence of *cis*-phosphine ligands is not unexpected since in other studies[6] we find that protonation of a variety of complexes of the type $Pt(CF_3C{\equiv}CCF_3)(PR_3)_2$ gives *cis*-phosphine platinum vinyl complexes $PtX(CF_3C{=}CHCF_3)(PR_3)_2$ ($PR_3 = PMePh_2$, PMe_2Ph, PEt_2Ph). The only exception to this is when PR_3 is triphenylphosphine since no P–F coupling is observed and the complex presumably has a *trans*-configuration about the platinum.[2,3,7] In recent related studies[4] it has also been shown that protonation of a variety of complexes Pt(alkyne)$(PPh_3)_2$ gives *trans*-phosphine complexes. It thus appears that electrophilic attack on zerovalent platinum hexafluorobut-2-yne occurs with retention of configuration about the double bond and, except when PR_3 is triphenylphosphine, with retention of configuration about the platinum.



(IV)

(X = Cl or Br)

We thank Johnson & Matthey Limited for the loan of platinum and the S.R.C. for grants (to D.M.B. and G.W.L.).

(*Received, December* 21*st*, 1970; *Com.* 2193.)

---

[1] R. D. W. Kemmitt and D. I. Nichols, *J. Chem. Soc.* (*A*), 1969, 1577.

[2] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Comm.*, 1969, 613.

[3] P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1970, **92**, 3825.

[4] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333.

[5] J. S. Valentine and D. Valentine, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 5795.

[6] R. D. W. Kemmitt and G. W. Littlecott, to be published.

[7] G. L. McClure and W. H. Baddley, *J. Organometallic Chem.*, 1970, **25**, 261.