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Preliminary communication

EVIDENCE FOR THE ELECTROPHILIC ADDITION OF ACID TO A COORDINATED ACETYLENE

HOWARD C. CLARK* and ANIL B. GOEL
Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario (Canada)

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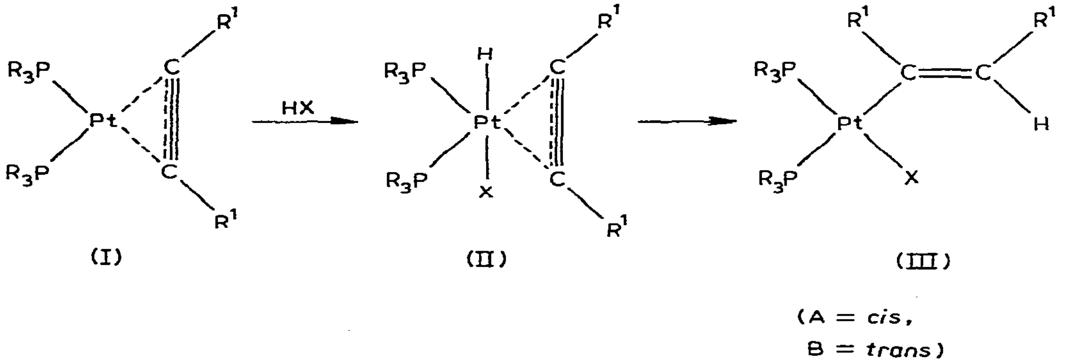
Summary

The reaction of acetic acid with $(Ph_3P)_2Pt(dma)$ (dma = dimethylacetylene dicarboxylate), in the presence of triphenylphosphine, proceeds by addition of triphenylphosphonium acetate across the acetylenic triple bond, rather than by oxidative addition of the acid to platinum.

Introduction

The reactions of protic acids with zerovalent acetylene-platinum complexes lead [1—4] to alkenyl derivatives. The mechanism is thought [5] to involve the formation, through oxidative addition of the acid, of six-coordinate platinum(IV) intermediates, which then undergo insertion into the Pt—H bond.



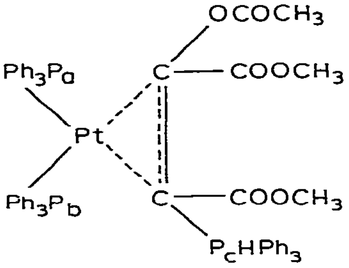
The process is obviously central to the metal-catalyzed reduction of acetylenes [6], for which both the coordination of the acetylene to the metal [7,8], and the formation of alkenyl-metal species [9] as intermediates have been postulated as important steps.

The evidence supporting the above postulated transformations from I → II and II → IIIA or IIIB, is scant, and such six coordinate platinum(IV) hydride species have not yet been characterized. Jonassen et al. [10], using non-iterative semi-empirical one-electron molecular-orbital calculations (NISEMO) suggested that the above pathway would be improbable and proposed [11,12] an alternative mechanism based on direct protonation of the complexed acetylene.

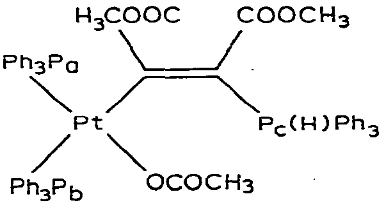
Results and discussion

We have attempted to isolate platinum(IV) hydrides of type II from the reactions of various halo-acetic acids, HX (where X = CF_3COO, Cl_3CCOO, Cl_2CHCOO, $ClCH_2COO$, and $BrCH_2COO$) with $(PR_3)_2Pt(dma)$ (where R = Ph or Cy, and dma = dimethylacetylene dicarboxylate). In all cases, products of type III were formed, these having the *cis*-geometry (IIIA) with PPh_3, and the *trans*-geometry (IIIB) with PCy_3. When acetic acid itself was added to complex I (R = Ph), there was essentially no reaction over a period of one week. Surprisingly, upon addition of one equivalent of triphenylphosphine, a reaction commenced immediately and was complete within two days. Most interestingly, the product differed from the vinylic species obtained in the previous reactions.

The product is a white solid, obtained in almost quantitative yield, whose analyses correspond to either IV or V.



(IV)

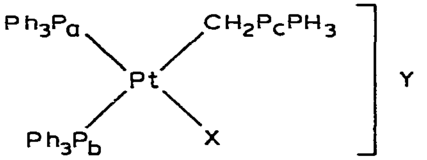


(V)

Compound IV would result from the direct addition of $[Ph_3PH]^+[OOCCH_3]^-$ across the acetylenic C≡C bond of I, while V could be formed by a reaction sequence similar to I → II → III. The following spectroscopic evidence argues in favour of the reaction product having structure IV. The infrared spectrum of the product shows strong absorptions at 1695 and 1700 cm^{-1} due to $\nu(C{=}O)$ and a weak band at ≃ 2340 cm^{-1} assignable to $\nu(P{-}H)$. In the 1500—1695 cm^{-1} region only a weak band at 1580 cm^{-1} is seen (phenyl absorption) suggesting the absence of C=C and thus favoring structure IV in preference to V. The proton NMR spectrum shows three singlets at δ 2.99, 3.45 and 2.11 ppm in a 1/1/1 intensity ratio. The first two resonances can be assigned to two non-equivalent $COOC\underline{H}_3$ groups, and the last to the CH_3 protons of an acetato group. Additionally a doublet is observed at δ 6.13 ppm, assignable to the proton attached to phosphorus, with $J(PH)$ 425 Hz; each component of the doublet is broadened slightly probably due to some coupling to ^{195}Pt. The ^{31}P NMR spectrum of the product shows three acts of resonances. A doublet at δ 20.35 ppm with $J(P_aP_b)$ 12.2 Hz (with satellites due to ^{195}Pt coupling $J(PtP_b)$ 4309 Hz) and a triplet at δ 24.34 ppm with two phosphorus—phosphorus couplings $J(P_aP_b)$ 12.2 Hz and $J(P_aP_c)$ 9.8 Hz and with the ^{195}Pt satellites $J(PtP_a)$ 3430 Hz can be assigned readily to the phosphorus nuclei of two *cis*-Ph_3P ligands. However, the magnitudes of the $J(PtP)$ values (both greater than 3400 Hz) are consistent with a zerovalent species (compound IV), whereas for compound V with Ph_3P *trans* to a vinylic group on a platinum(II) centre, $J(PtP) \leqslant 2000$ Hz is expected. Furthermore, the set of resonances at δ 24.34 ppm, essentially a triplet, can be explained in terms of IV as caused by a *cis* coupling with Ph_3P_b, $^2J(P_aP_b)$ 12.2 Hz, and a *trans* coupling with $Ph_3H(C)P_c$, $^3J(P_aP_c)$ 9.8 Hz, structure V does not provide such a ready interpretation. The third set of signals consists essentially of a doublet at δ 29.85 ppm ($^3J(P_cP_a)$ 9.8 Hz) with satellites due to ^{195}Pt coupling with an exceptionally small value of $J(PtP_c)$ 100 Hz. Such data are consistent with a two bond coupling between ^{195}Pt and the phosphorus nucleus of the phosphonium group of IV.

The above assignments for the ^{31}P NMR spectrum can be compared with data for related compounds. Thus, the ^{31}P spectrum of $(Ph_3P)_2Pt$(dma) shows a resonance at δ 21.51 ppm with $J(PtP)$ 3728 Hz and the related ethylene complex, $(Ph_3P)_2Pt(C_2H_4)$ gives $\delta(P)$ 31.56 ppm with $J(PtP)$ 3723 Hz. In contrast, $J(PtP)$ values for phosphorus *trans* to carbon in platinum(II) complexes are usually $\leqslant 2000$ Hz, e.g. the vinylic complex IIIA ($X = CF_3COO$) shows two ^{31}P resonances at $\delta(P_1)$ 6.68 ppm with $J(PtP_1)$ 4319 Hz and $J(P_1P_2)$ 17.1 Hz, and $\delta(P_2)$ 18.90 ppm with $J(PtP_2)$ 1992 Hz and $J(P_1P_2)$ 17.1 Hz. The first resonance is assigned to the phosphorus *trans* to CF_3COO and the latter to phosphorus *trans* to the vinylic group.

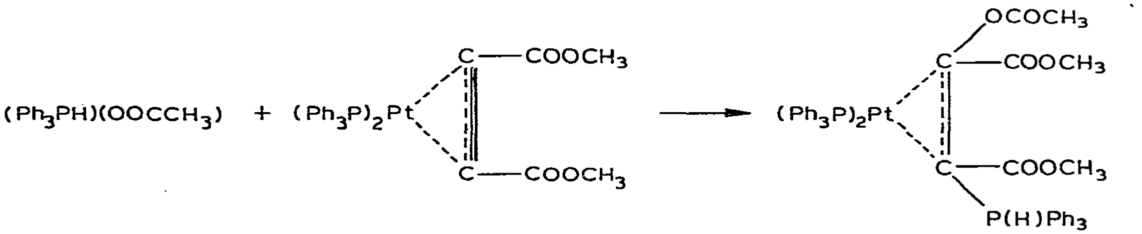
That the above data for the reaction product are in accord with IV, rather than V, is further supported by the very recent report [13] of the preparation of the ylide-platinum(II) complex (VI), which is closely related to V. The ^{31}P spectrum of VI is very different from that described above for our reaction product.



VI

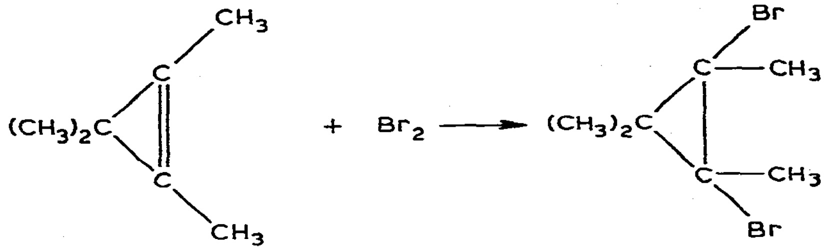
The product is thus considered to be the formally zerovalent platinum olefinic complex, IV, formed by the addition of phosphonium acetate across the acetylenic C≡C bond of I, as shown below:

$$Ph_3P + CH_3COOH \rightleftharpoons [Ph_3PH]^+ [OOCCH_3]^-$$

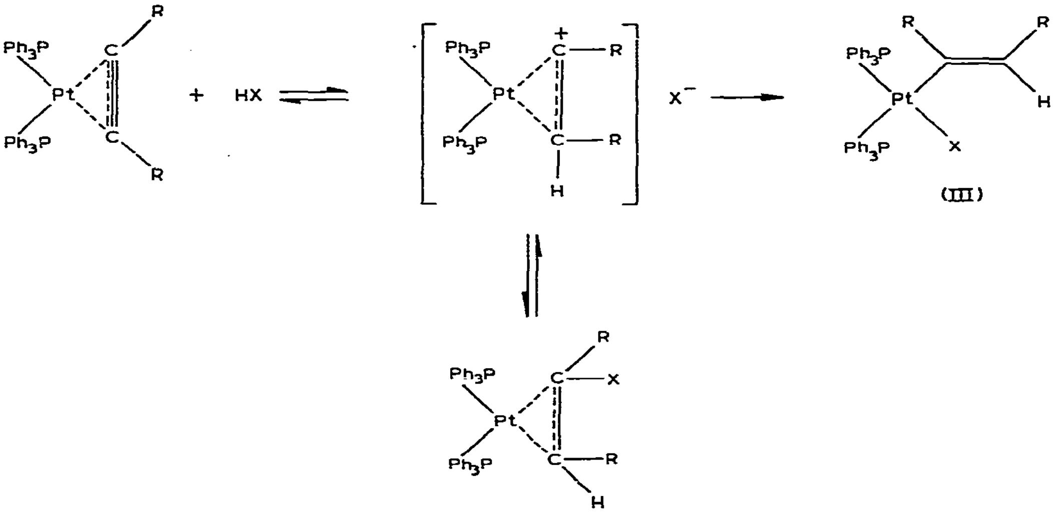


Such an addition across the coordinated acetylenic bond, with preservation of the three-membered metallocycle, is similar to the halogenation (e.g. bromination) of cyclopropenes [14].

e.g.



By analogy, the complexes I might then be regarded as "platinirenes". Reactions with acids, HX, would then generally occur, as in cyclopropenes, by the direct addition of HX across C≡C to give "platinirene". Subsequent rearrangement, through nucleophilic attack by X, of the remaining carbonium ion leads to the vinyl complex [15—17].



(III)

(IV)

However, the extent to which IV is sufficiently stable to be isolated obviously depends on X^-. Thus, the reaction of $(Ph_3P)_2Pt(dma)$ with $Cl_2CHCOOH$ in the presence of Ph_3P gives the vinylic product III and $Ph_3PH^+Cl_2CHCOO$ but no IV.

It might be suggested that, in accordance with some of Jonassen's proposals [10—12], the first step is the displacement of acetylene from platinum, induced by the presence of added phosphine.

$(Ph_3P)_2Pt(dma) + Ph_3P \rightarrow (Ph_3P)_3Pt + dma$. However, the fact that by ^{31}P NMR spectroscopy no reaction can be detected between complex I and added phosphine, rules out this possibility.

Acknowledgements

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