CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORIES,
TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA 70118

# Platinum–Acetylene Complexes. II. Monosubstituted Hydroxyacetylenes[1,2]

BY JOHN H. NELSON, H. B. JONASSEN, AND D. M. ROUNDHILL

*Received May 1, 1969*

The reactions of some $\alpha$-hydroxyacetylenes with the complexes tetrakis(triphenylphosphine)platinum(0), I, and *cis*-dichlorobis(triphenylphosphine)platinum(II), II, have been studied. Reaction of either I or II under appropriate conditions with 1-ethynylcyclopentanol, 1-ethynylcyclohexanol, 1-ethynylcycloheptanol, 3-methyl-1-butyn-3-ol, 1,1-diphenyl-2-propyn-1-ol, and 3-methyl-1-pentyn-3-ol yielded complexes containing $\mu$-bonded acetylenes. The C≡C stretching frequency of the complexed acetylene in the infrared spectrum is lowered by about 400 $cm^{-1}$ over that of the free acetylene and the acetylenic proton appears in the nmr spectrum as an AA'MX type of multiplet centered at $\tau \sim 3.7$ ppm. Mechanistic implications are presented and discussed.

## Introduction

A considerable number of mononuclear complexes of transition metals in low- or zero-oxidation states and various acetylenes have been reported.[3–5] Very often several products have resulted from these reactions; among them were binuclear and polynuclear complexes as well as acetylene polymerization products. Very little attention has been given to the influence of steric and electronic effects of the acetylenes on the nature of the mononuclear products of platinum(IV)–, platinum(II)–, and platinum(0)–acetylene complexes, which have been known for some time.[3–10] Only one study of electronic effects[9] concerning platinum acetylene complexes has appeared in the literature. Chatt, *et al.*,[7] prepared platinum(II) complexes of dihydroxyacetylenes and found that the hydroxy groups as well as the acetylene participated in bonding. The isolation of bisacetylide complexes[3,10] led to the decision to undertake a systematic study of the steric and electronic influences of the acetylenes on the structure of platinum-acetylene complexes. The first part of this study using a series of monosubstituted hydroxyacetylenes is reported herein.

## Experimental Section

**A. Reagents and Physical Measurements.**—3-Methyl-1-butyn-3-ol (Aldrich), 1-ethynylcyclohexanol (Matheson Coleman and Bell), 1-ethynylcyclopentanol (Farchan Research Laboratories), and 3-methyl-1-pentyn-3-ol (K & K Laboratories) were used without further purification. 1-Ethynylcycloheptanol was prepared from cycloheptanone by the method of Dominguez and Garza.[11] 1,1-Diphenyl-2-propyn-1-ol was prepared from benzophenone and lithium acetylide ethylenediamine (Foote Chemical) by the method of Beumel and Harris.[12]

All solvents were purified and freed from water by standard procedures and stored over Linde 3A molecular sieves for at least 2 days prior to use. Tetrakis(triphenylphosphine)platinum(0)[13] and *cis*-dichlorobis(triphenylphosphine)platinum(II)[14] were prepared according to literature procedures.

Infrared spectra were recorded on a Beckman IR-8 infrared spectrometer as KBr pellets for the complexes and as neat liquids for the acetylenes. Proton nmr spectra were obtained on the Varian Associates Model A-60 as deuteriochloroform solutions with tetramethylsilane as internal standard. Melting points were determined in the air and are uncorrected. Elemental analyses were performed either by Alfred Bernhardt Laboratorium, Mülheim, Germany, or Galbraith Laboratories, Knoxville, Tenn. They are listed in Table I.

**B. Preparation of the Complexes. 1. 1-Ethynylcyclohexanolbis(triphenylphosphine)platinum(0).**—The two following methods were used to prepare this $\mu$-bonded acetylene complex.

**Method I.**—To 0.60 g of $((C_6H_5)_3P)_4Pt$ suspended in 30 ml of nitrogen-degassed anhydrous ether was added 5 ml of 1-ethynylcyclohexanol (nitrogen degassed). The flask was stoppered and stirred magnetically under nitrogen. After 3 hr a colorless precipitate formed, which was filtered, washed with 20 ml of anhydrous ether, and dried under vacuum over $P_4O_{10}$. The yield was 0.320 g (79%) of colorless crystals, mp 142–143° dec.

**Method II.**—To a suspension of 0.3010 g of *cis*-$Cl_2Pt((C_6H_5)_3P)_2$ in 3 ml of absolute ethanol was added anhydrous hydrazine (97+%, MCB) dropwise until dissolution was *nearly* complete. (At the point of complete solution an unreactive yellow compound will precipitate. The nature of this yellow compound is not certain but is thought to be an immine-bridged platinum dimer.[15]) The solution was then quickly filtered by suction and 3 ml of 1-ethynylcyclohexanol was added. This solution was heated just to reflux and allowed to cool slowly while being stirred magnetically for 2–3 hr. The resultant colorless microcrystalline precipitate (0.1000 g, 33.4%) was filtered, washed with 10 ml of absolute ethanol and 10 ml of anhydrous ether, and dried for several hours under reduced pressure over $P_4O_{10}$; mp 142–143° dec. These complexes were recrystallized by solution in a minimum of cold nitrogen-degassed anhydrous benzene. To this solution was added an equal volume of anhydrous methanol and the benzene was evaporated without heating under a stream of nitrogen to incipient precipitation.

---

[1] Part I: D. M. Roundhill and H. B. Jonassen, *Chem. Commun.*, 1233 (1968).

[2] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., 1969; see Abstracts, No. INOR 103.

[3] I. Wender and P. Pino, "Organic Synthesis *via* Metal Carbonyls," Interscience Publishers, New York, N. Y., 1968, and references contained therein.

[4] J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," American Elsevier, New York, N. Y., 1968, and references contained therein.

[5] R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968), and references contained therein.

[6] E. O. Greaves, C. J. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

[7] J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, *J. Chem. Soc.*, 5170 (1963).

[8] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[9] A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964).

[10] M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc., A*, 356 (1968).

[11] J. A. Dominguez and M. R. Garza, *Ciencia* (Mex.), **20**, 134 (1960); *Chem. Abstr.*, **55**, 18627*d* (1961).

[12] O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **29**, 1872 (1964).

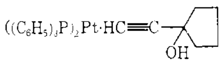
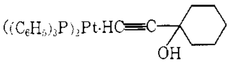
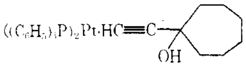
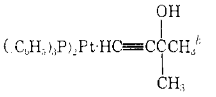
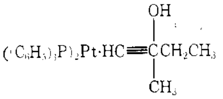
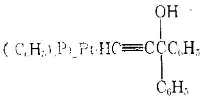
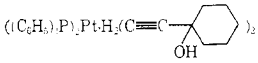
[13] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

[14] J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).

[15] G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, B. Morelli, S. Cenini, and F. Bonati, *Chem. Commun.*, 739 (1967).

Table I

Elemental Analyses and Physical Properties

| Complex | Mp,[a] °C | % carbon Calcd | % carbon Found | % hydrogen Calcd | % hydrogen Found | % phosphorus Calcd | % phosphorus Found | Prepn method |
|---|---|---|---|---|---|---|---|---|
|  | 148–150 | 62.11 | 61.93 | 4.86 | 4.87 | 7.34 | 7.46 | I and II |
|  | 142–143 | 62.62 | 62.41 | 5.02 | 5.02 | 7.22 | 7.22 | I and II |
|  | 151–153 | 63.50 | 63.81 | 5.10 | 5.16 | 7.12 | 7.35 | I and II |
|  $((C_6H_5)_3P)_2Pt\cdot HC\equiv C\overset{OH}{\underset{CH_3}{C}}CH_3$[b] | 147–149 | 61.08 | 61.36 | 4.88 | 4.92 | 7.70 | 8.00 | I and II |
|  $((C_6H_5)_3P)_2Pt\cdot HC\equiv C\overset{OH}{\underset{CH_3}{C}}CH_2CH_3$ | 144–147 | 61.10 | 61.56 | 5.01 | 4.86 | 7.68 | 7.84 | I and II |
|  $((C_6H_5)_3P)_2Pt\cdot HC\equiv C\overset{OH}{\underset{C_6H_5}{C}}C_6H_5$ | 178–180 | 66.10 | 66.35 | 4.56 | 4.50 | 6.67 | 6.87 | I and II |
|  | 249–252 | 64.53 | 64.46 | 5.73 | 5.65 | 6.40 | 6.34 | I |

[a] All complexes melted with decomposition. [b] Per cent platinum: calcd, 24.25; found, 24.57.

2. *trans*-**Dihydridobis(triphenylphosphine)bis(1-ethynylcyclohexanol)platinum(IV).**[1]—To 0.60 g of tetrakis(triphenylphosphine)platinum(0) suspended in 30 ml of nitrogen-degassed ether was added 3 ml of 1-ethynylcyclohexanol under nitrogen. The flask was stoppered and allowed to stand for 4 days. The initially yellow suspension gradually dissolved to form a colorless solution with the slow deposition of colorless crystals. After 4 days the solution was concentrated to half-volume by aspiration at room temperature, filtered, washed with 10 ml of anhydrous ether, and dried under reduced pressure over $P_4O_{10}$ to yield 0.0815 g (17.5%) of colorless crystals, dec pt 249–252°.

3. *trans*-**Hydridochlorobis(triphenylphosphine)platinum(II).**—To a solution of *trans*-dihydridobis(triphenylphosphine)bis(1-ethynylcyclohexanol)platinum(IV) (prepared as above) in ether was added 5 ml of carbon tetrachloride and the solution was stirred for 2 days. A colorless precipitate formed which was filtered, washed with ether, and dried under reduced pressure over $P_4O_{10}$; dec pt 200–205°, lit.[14] value 210–215°. *Anal.* Calcd for $C_{36}H_{31}ClP_2Pt$: C, 57.03; H, 4.09; P, 8.44; Cl, 4.68; Pt, 25.74. Found: C, 56.85; H, 4.14; P, 8.59; Cl, 4.97; Pt, 26.50.

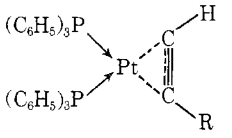
4. **Tripropynylhydrazine Hydrobromide.**—*cis*-Dichlorobis(triphenylphosphine)platinum(II) was suspended in ethanol and anhydrous hydrazine was added dropwise until solution was nearly complete and the solution was filtered. To the filtrate was added 3-bromopropyne (Aldrich) dropwise. There was an immediate exothermic reaction with gas evolution. The reaction mixture was stirred for 1 hr and the white crystals which formed were filtered, washed with ethanol, and dried under vacuum over $P_4O_{10}$; mp 88–90°. *Anal.* Calcd for $N_2H_5Br$: N, 24.8; H, 4.43; Br, 70.8. Found: C, 0.47; N, 24.48; H, 4.57; Br, 70.18. The nmr spectrum possesses only one peak and the infrared spectrum is very similar to that of hydrazine dihydrochloride.

The filtrate from the above reaction was heated just to boiling and stirred for 24 hr. A yellow solution formed and after 48 hr large white crystals precipitated. These were filtered, washed with ethanol and ether, and dried under reduced pressure over $P_4O_{10}$; mp 149–152°. *Anal.* Calcd for tripropynylhydrazine hydrobromide, $C_9H_{11}N_2Br$: C, 47.6; H, 4.84; N, 12.3; Br, 35.2. Found: C, 46.99; H, 4.76; N, 12.14; Br, 34.43.

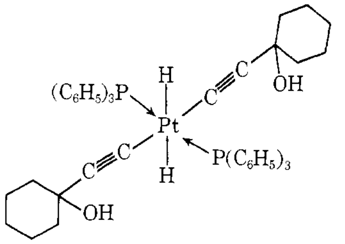
Hydrazine and 3-bromopropyne were also allowed to react in the absence of platinum under conditions otherwise identical with those above but hydrazine hydrobromide was the only crystalline product isolated.

## Results

The elemental analyses (Table I), infrared spectral data (Table II), and pmr data (Table III) indicate that the reactions of either tetrakis(triphenylphosphine)platinum(0) or *cis*-dichlorobis(triphenylphosphine)platinum(II) with hydroxyacetylenes yield stable platinum complexes having the stoichiometry $[Pt((C_6H_5)_3P)_2(HC_2R)]$ (type A). However, 1-ethynylcyclohexanol also reacts with tetrakis(triphenylphosphine)platinum(0) to yield a complex B with the $[Pt((C_6H_5)_3P)_2(HC_2R)_2]$ stoichiometry.[1]



A

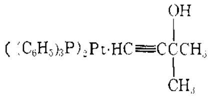
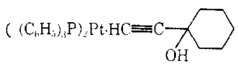
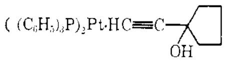
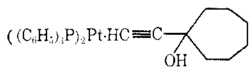
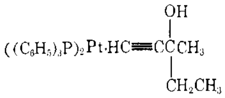
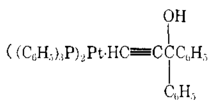
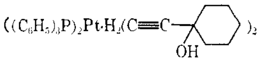


B

The infrared spectra of type A complexes do not show a band in the region of $\nu_{C\equiv C}$ but show a new band around 1680 cm$^{-1}$ (Table II) attributable to $\nu_{C=C}$, indicating that the carbon–carbon triple bond has been reduced essentially to a double bond. The magnitude

TABLE II

INFRARED SPECTRAL DATA FOR THE COMPLEXES

| Complex | $\nu_{OH}$, cm$^{-1}$ |  | $\nu_{C\equiv C}$, cm$^{-1}$ |  |
|---|---|---|---|---|
|  | Free ligand | Complex | Free ligand | Complex |
|  $((C_6H_5)_3P)_2Pt\cdot HC{\equiv}C\overset{OH}{\underset{CH_3}{C}}CH_3$ | 3620 | 3570 | 2114 | 1681 |
|  | 3620 | 3575 | 2117 | 1686 |
|  | 3620 | 3575 | 2120 | 1681 |
|  | 3440 | 3180 | 2120 | 1668 |
|  $((C_6H_5)_3P)_2Pt\cdot HC{\equiv}C\overset{OH}{\underset{CH_2CH_3}{C}}CH_3$ | 3450 | 3390 | 2125 | 1670 |
|  $((C_6H_5)_3P)_2Pt\cdot HC{\equiv}C\overset{OH}{\underset{C_6H_5}{C}}C_6H_5$ | 3540 | 3400 | 2118 | 1678 |
|  | 3620 | 3620 | 2117 | 2120 |

of the shift in $\nu_{C\equiv C}$ is among the largest yet reported for acetylene complexes. The infrared spectrum of B showed a medium intensity peak at 2120 cm$^{-1}$ which represents both $\nu_{C\equiv C}$ and $\nu_{Pt-H}$.[16] This peak is however predominantly $\nu_{Pt-H}$ as the complex prepared from deuterio-1-ethynylcyclohexanol showed only a *very weak* peak at 2120 cm$^{-1}$.

The O–H stretching frequency, $\nu_{OH}$, for type A complexes is shifted to lower energy relative to that of the free acetylene by 45–260 cm$^{-1}$ while for type B complexes $\nu_{OH}$ remains unchanged. Some type of hydrogen bonding of the hydroxyl groups in type A complexes is thus indicated; however, the OH resonance is found at higher field in the pmr spectra of type A and type B complexes than for the free acetylenes indicating less association of the hydroxyl group in the complexes than in the free acetylenes. Chatt, *et al.*,[7] found that for platinum(II)–dihydroxyacetylene complexes of the type K[PtCl$_3$RC$_2$R], $\nu_{OH}$ shifted to lower energy by 110–140 cm$^{-1}$ and that the proton resonance of the hydroxyl proton shifted downfield by 1.5$\tau$, both consistent with hydrogen-bond formation with the chlorine atoms OH---Cl upon coordination. Apparently platinum(0) interacting with the hydroxyl group causes a lowering in $\nu_{OH}$ while at the same time it shields the hydroxyl proton.

The pmr spectra of type A complexes have the following general features: an unresolved multiplet centered at $\tau$ 2.7 (phenyl), a singlet in the range $\tau$ 8.3–9.2 (OH), and a multiplet consisting of at least four resolvable peaks centered at $\tau$ 3.7 (C≡C—H). The C≡C—H $\tau$ value in the vinyl region is consistent with the C═C absorption in the infrared spectrum indicating that the coordinated acetylene is nearly equivalent to an alkene. A typical spectrum is shown in Figure 1.

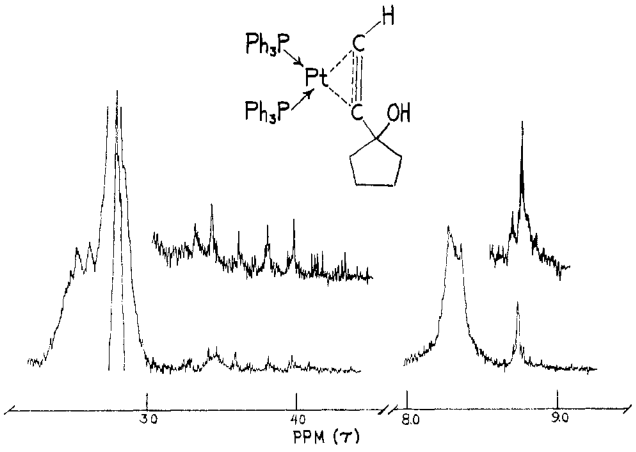


Figure 1.—The 60-Mz spectrum of a typical type A complex in CDCl$_3$. $\tau$ values are relative to the TMS internal standard.

The C≡C—H resonance may be interpreted as an AA′MX multiplet arising from coupling with platinum-195 (nuclear spin $I = {}^1/_2$, 34% natural abundance) and coupling with the two nonequivalent phosphorus-31 nuclei. Theoretically this would give rise to an apparent sextet with intensity ratios of 1:5:6:6:5:1. The experimental intensity ratios of the four resolved peaks are about 1:1:1:1. The two outside members of the multiplet are not resolved. This may be because this resonance saturates very easily and these peaks are anticipated to be weak (only one-sixth of the most intense peaks). The coupling constants obtained from the interpretation of these spectra are: $J_{Pt-H} = 22 \pm 1$ Hz, $J_{P-trans-H} = 10 \pm 1$ Hz, and $J_{P-cis-H} < 2$ Hz. The AA′MX pattern has been previously observed for the methyl group in the compound[17] ((C$_6$H$_5$)$_3$P)$_2$Pt·CH$_3$C≡CC$_6$H$_5$ with $J_{Pt-H} = 41.5$ Hz, $J_{P-trans-H} = 6.2$ Hz, and $J_{P-cis-H} \cong 1$–2 Hz and for similar complexes of other methyl acetylenes.[18] This pattern has also been observed by $^{19}$F nmr for the CF$_3$ group in the complex[19] ((C$_6$H$_5$)$_3$P)$_2$Pt·CF$_3$C≡CCF$_3$ where $J_{Pt-F} = 65.1$ Hz and $J_{P-F} = 10.3$ Hz. As pointed out by one of the referees the exact analyses of this coupling could best be determined by the use of a 100-MHz nmr spectrometer, which investigation is in progress with the cooperation of an investigator in another institution.

The pmr spectrum of type B complexes shows three resonances. The two lower field ones consist of unresolved multiplets centered at $\tau$ 2.39 (phenyl) and $\tau$ 9.05 (CH$_2$) with relative areas confirming the presence of one acetylene for each triphenylphosphine. The third resonance occurs at $\tau$ 22.88 and can only be due to the hydridic hydrogen.

The hydroxyl resonance is not resolved and must have shifted upfield from that of the free acetylene into

---

[16] P. W. Atkins, J. C. Green, and M. L. H. Green, *J. Chem. Soc., A*, 2275 (1968).

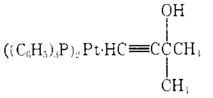
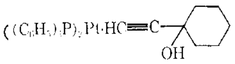
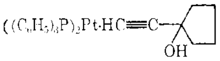
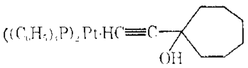
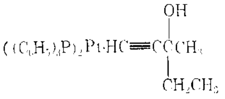
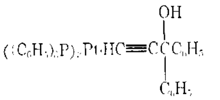
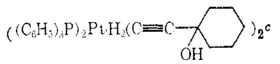
[17] E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

[18] J. H. Nelson and H. B. Jonassen, unpublished results.

[19] J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 3408 (1963).

TABLE III

NMR SPECTRAL DATA FOR THE COMPLEXES

| Complex | τ values, ppm | | | | |
|---|---|---|---|---|---|
| | $C_6H_5$ | $CH_2$ | C-H | OH | $CH_3$ |
|  $((C_6H_5)_3P)_2Pt\cdot HC{\equiv}CC(OH)(CH_3)CH_3$ | 2.70 | . . . | 3.76 | 8.34 | 8.68[a] |
|  | 2.68 | 8.50 | 3.74 | 8.75 | . . . |
|  | 2.70 | 8.32 | 3.72 | 8.75 | . . . |
|  | 2.70 | 8.49 | 3.78 | 8.98 | . . . |
|  $((C_6H_5)_3P)_2Pt\cdot HC{\equiv}CC(OH)(CH_2CH_3)CH_3$ | 2.70 | 8.46 | 3.78 | 9.20 | 8.75,[a] 9.17[b] |
|  $((C_6H_5)_3P)_2Pt\cdot HC{\equiv}CC(OH)(C_6H_5)C_6H_5$ | 2.80 | . . . | 3.55 | 8.80 | . . . |
|  | 2.39 | 9.05 | . . . | d | . . . |

[a] Triplet, $J_{Pt-H} = 2.3$ Hz. [b] Triplet of triplets, $J_{H-H} = 6.5$ Hz, $J_{Pt-H} \leq 1$ Hz. [c] $\tau_{Pt-H}$ 22.88. [d] Obscured by $CH_2$ resonance.

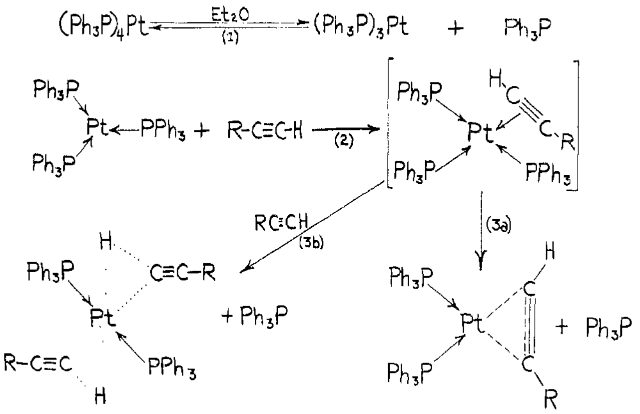


Figure 2.—Proposed mechanism for reaction of $((C_6H_5)_3P)_4Pt$ with acetylenes.

the methylene region, a shift which is in the same direction as for type A complexes. Upon addition of $D_2O$ to the deuteriochloroform solution the integrated intensity of the methylene resonance decreases by an amount corresponding to two protons further suggesting that the hydroxyl resonance is buried under the methylene resonance.

The mass spectral breakdown pattern of type A complexes showed only the breakdown pattern of triphenylphosphine. The pattern of B possesses fragments due to breakdown of the acetylene, fragments due to triphenylphosphine, and three weak peaks at *m/e* 196, 197, and 198 which are the $PtH_2$ fragments for the three isotopes of platinum. The relative intensities of the $PtH_2$ peaks are in close agreement with the natural isotopic abundance of platinum.

The *trans* structure of B is further supported by the isolation of *trans*-$((C_6H_5)_3P)_2PtHCl$ from the reaction of B with carbon tetrachloride (*vide supra*). This compound was identified by chemical analyses and by comparing the infrared spectra with that reported by Bailar and Itatani[14] ($\nu_{Pt-H}$ 2220 $cm^{-1}$ in KBr; lit. value 2220 $cm^{-1}$).

## Discussion

Preparation method I yields two different types of acetylene complexes depending upon the steric nature of the acetylene.[1] Relatively small unhindered acetylenes form a μ-bonded platinum(0)-acetylene complex (type A) while sterically hindered acetylenes form platinum(IV) acetylide hydride complexes (type B) in addition to the type A complexes. With an excess of triphenylphosphine type A complexes are formed with all of the acetylenes studied. Type A complexes are also formed in this reaction when methanol, ethanol, or water is added to the ethereal solutions of $Pt((C_6H_5)_3P)_4$ and the acetylenes. However, if acetic acid is added to the ethereal solutions, type B complexes result.

1-Ethynylcyclopentanol seems to be on the borderline in steric requirement as both complex types have been formed with this acetylene by method I without excess triphenylphosphine. A full discussion of the platinum acetylide hydride complexes is in preparation.

The proposed reaction mechanism for these reactions is presented in Figure 2. In equilibrium 1, $((C_6H_5)_3P)_4$-Pt has been shown to be completely dissociated[20] to $((C_6H_5)_3P)_3Pt$; further dissociation to $((C_6H_5)_3P)_2Pt$ is

---

(20) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968).

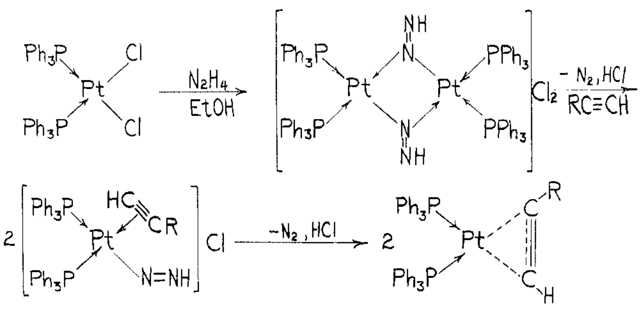


Figure 3.—Proposed mechanism for reaction of *cis*-$Cl_2Pt((C_6H_5)_3P)_2$ with acetylenes.

slight. $((C_6H_5)_3P)_3Pt$, which has been shown by X-ray structure determination to have the trigonal-planar structure,[21] can be assumed to be the reactive species. It is a coordinatively unsaturated complex and can react readily with an acetylene (step 2). For a bulky acetylene *trans* labilization of $(C_6H_5)_3P$ occurs (before rotation of the acetylene followed by *cis* labilization) and the platinum(IV) acetylide hydride complex (B) is formed (step 3b) by addition of a second molecule of acetylene. Hydroxyacetylenes have been shown to be better *trans* directors than triphenylphosphine.[22] Hydride transfer could then proceed either simultaneously or subsequent to platinum–carbon bond formation.

On the other hand, for a small unhindered acetylene, rotation and *cis* labilization occurs before *trans* labilization and the $\mu$-bonded acetylene complex (type A) is formed. All of the presently available data are consistent with this mechanism which is similar to that proposed for nickel-catalyzed oligomerization of acetylenes.[23,24]

Preparation method II yields the $\mu$-bonded acetylene complexes (type A) irrespective of the steric factors of the acetylene. Figure 3 illustrates a mechanism consistent with these results. It has been shown that hydrazine reduction of *cis*-$Cl_2Pt((C_6H_5)_3P)_2$ proceeds through several steps,[15] one of which is the first illustrated in Figure 3. The hydrazine-bridged intermediate (C) loses nitrogen very readily, and upon further addition of hydrazine *trans*-$Pt((C_6H_5)_3P)_2HCl$ is formed.[15] Prior to the precipitation of *trans*-$Pt((C_6H_5)_3P)_2HCl$, a yellow compound suspected to be the immine-bridged dimer (D) is formed.[15] An X-ray structural determination of the compound thought to be C showed it to be a mixture of C and D. This yellow compound (D?) does not react with hydroxyacetylenes (*vide supra*). The postulate of intermediate C is further supported by the observation that 3-bromopropyne reacts with an ethanol solution of II and hydrazine to form hydrazine hydrobromide and tripropynylhydrazine hydrobromide.[25] Hydrazine, however, reacts with 3-bromopropyne to form only hydrazine hydrobromide under the same conditions. It is thus reasonable to assume that C also is an intermediate in this reaction. Since it is not possible at this time to distinguish between symmetrical and unsymmetrical cleavage of C, only the symmetrical mechanism, which the authors favor, is illustrated.

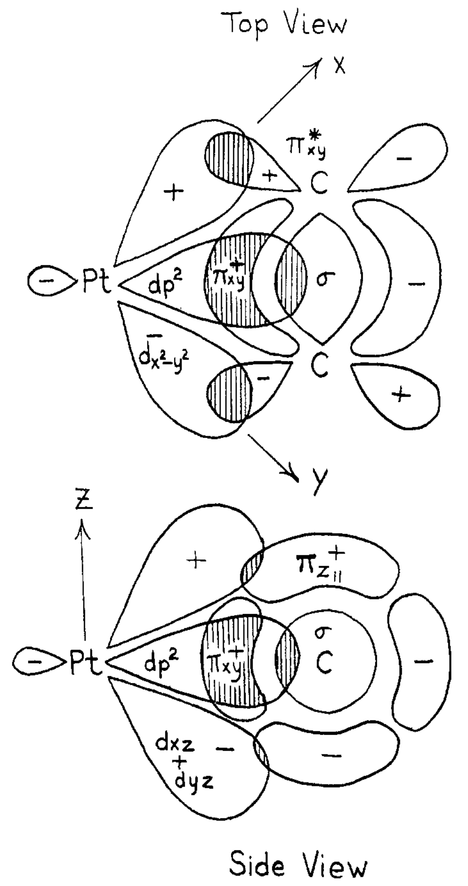
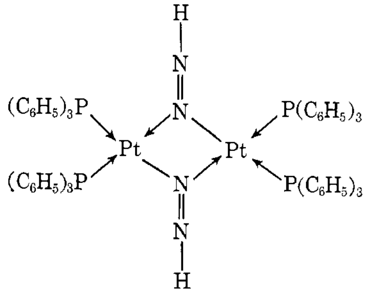
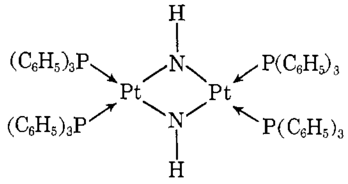


Figure 4.—Orbitals participating in bonding for metal–acetylene complexes.



C



D

---

[21] V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966).

[22] T. P. Cheeseman, A. L. Odell, and H. A. Raethel, *ibid.*, 1496 (1968).

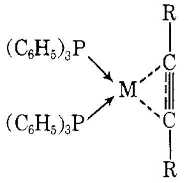
[23] L. S. Meriwether, F. G. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **26**, 5155 (1961).

[24] L. S. Meriwether, M. F. Leto, E. G. Colthup, and G. W. Kennerly, *ibid.*, **27**, 3930 (1962).

(25) The identity of these two compounds was established by elemental analyses and infrared and nmr spectra. Pertinent data for tripropynylhydrazine hydrobromide follow: infrared (KBr disk), $\nu_{C\equiv C}$ at 2120 cm$^{-1}$ (strong); the nmr in DMSO-$d_6$ with DSS internal reference showed five peaks—a quintet at $\tau$ 7.44 (DMSO-$d_5$), a broad singlet at $\tau$ 6.52 ($H_2O$ in DMSO), a doublet at $\tau$ 5.29 ($CH_2$, $J$ = 2Hz), a triplet at $\tau$ 5.84 (C≡C—H, $J$ = 2 Hz), and a broad singlet at $\tau$ 3.58 (NH). The integrated intensities were in the ratio 6:3:2 for ($CH_2$):(C≡C—H):(NH).

Recently one-electron semiempirical molecular orbital calculations were performed[26,27] on a series of platinum–acetylene and –olefin complexes in order to ascertain the mode of bonding and to explain the physical properties of the complexes. Calculations were performed for two configurations, planar and pseudotetrahedral. The calculations clearly illustrate that the complexes are best represented by three-coordinate platinum(0) with $dp^2$ hybridization in the planar case and $d^2p$ hybridization in the pseudotetrahedral case. A bonding scheme, derived with the aid of group theory, that is consistent with the molecular orbital calculations is shown in Figure 4.

Greaves, Lock, and Maitlis[6] have come to the same conclusion about the bonding in acetylene complexes based upon molecular orbital arguments and they proposed that the complexes should best be represented by



E

a formula which appears to be the least misleading.

The calculations indicate that upon coordination the acetylenic hydrogen becomes negatively charged which is in accordance with the observation that reaction of I with acetylenes in the presence of methanol, ethanol, or water yields type A complexes whereas in the presence of acetic acid type B complexes are formed.

The planar and pseudotetrahedral configurations were found to differ only slightly in energy. Thus the complexity of the C≡C—H resonance in the pmr spectra might possibly be explained by the presence of both forms in solution.[28] Further work along these lines is now in progress.

**Acknowledgment.**—We thank Dr. M. Gordon and Dr. L. C. Cusachs for their helpful and stimulating discussions concerning this work and Mr. Gordon Boudreaux for obtaining the pmr spectra. The financial support of the Esso Research Laboratories, Humble Oil and Refining Co., Baton Rouge, La., is gratefully acknowledged. We appreciate the assistance provided by the National Science Foundation through Chemistry Research Instrument Grants GP-1690, GP-5203, GP-6915, and GP-8237.

---

[26] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Commun.*, 1019(1969).

[27] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Am. Chem. Soc.*, in press.

(28) NOTE ADDED in PROOF.—The acetylene in these complexes exchanges slowly [6,18,20] according to the reaction

$$Pt[(C_6H_5)_3P]_2(RC_2H) + CDCl_3 \longrightarrow Pt[(C_6H_5)_3P]_2Cl(CDCl_2) + RC_2H$$

as shown by the slow appearance of peaks attributable to free acetylene.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EMORY UNIVERSITY, ATLANTA, GEORGIA 30322

# *cis* and Charge Effects in Platinum(II)-Catalyzed Substitution Reactions of Platinum(IV) Complexes

BY SUSAN G. BAILEY AND RONALD C. JOHNSON

*Received May 8, 1969*

Reactions of the type *trans*-$Pt(NH_3)_4Cl_2^{2+}$ + $Pt(dien)A^{n+}$ + $2Br^-$ → *trans*-$Pt(dien)ABr_2^{n+}$ + $Pt(NH_3)_4^{2+}$ + $2Cl^-$ and $Pt(dien)Br^+$ + *trans*-$Pt(dien)ACl_2^{n+}$ + $2Br^-$ → *trans*-$Pt(dien)Br_3^+$ + $Pt(dien)A^{n+}$ + $2Cl^-$ (where A = $NO_2^-$, $Br^-$, or $NH_3$; $n$ = 1 or 2; dien = diethylenetriamine) were found to have third-order rate laws, with first-order rate dependences on the reactant Pt(IV) complex, the reactant Pt(II) complex, and bromide ion concentrations. The fastest reaction was less than ten times faster than the slowest, which indicates that *cis* and charge effects are relatively minor. The relative rates parallel the ease of oxidation of $Pt(dien)A^{n+}$ and of reduction of *trans*-$Pt(dien)ACl_2^{n+}$. The rate data are interpreted in terms of a bridged inner-sphere redox mechanism involving an activated complex of the type Pt–Cl–Pt. Rate constants and activation parameters are reported. Equilibrium constants related to these reactions were studied spectrophotometrically and correlated with the rate data.

## Introduction

Numerous papers have appeared in recent years concerning detailed aspects of substitution reactions of platinum(IV) cations.[1–9] For these reactions, the observed first-order rate dependence on the concentrations of the platinum(IV) complex, the entering halide ion, and a platinum(II) complex is consistent with a mechanism proposed by Basolo and Pearson[2] involving an inner-sphere two-electron transfer followed by

---

[1] F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

[2] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).

[3] W. R. Mason, III, and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965).

[4] R. C. Johnson and E. R. Berger, *ibid.*, **4**, 1262 (1965).

[5] R. R. Rettew and R. C. Johnson, *ibid.*, **4**, 1565 (1965).

[6] W. R. Mason, III, E. R. Berger, and R. C. Johnson, *ibid.*, **6**, 248 (1967).

[7] R. C. Johnson and E. R. Berger, *ibid.*, **7**, 1656 (1968).

[8] A. Peloso and G. Dolcetti, *Coord. Chem. Rev.*, **1**, 100 (1966).

[9] A. Peloso and G. Dolcetti, *Gazz. Chim. Ital.*, **97**, 120 (1967).