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Reactions of Palladium(0)-Phosphine Complexes with Terminal α -Hydroxyacetylenes¹

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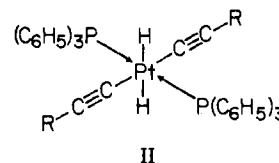
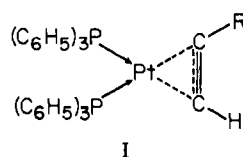
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The reactions of acetylenes with the zerovalent palladium complexes $(PPh_3)_nPd$, where $n = 3$ or 4, and $(R_3P)_2Pd(C_2H_4)$, where $R_3P = (CH_3)_2PC_6H_5$ or Ph_3P , have been studied. It was found that terminal acetylenes react with these complexes to produce the air-stable colorless crystalline complexes $trans-(R_3P)_2Pd(C\equiv CR)_2$ in reasonable yield. No complexes could be isolated from reactions with nonterminal acetylenes; rather uncharacterizable "thick black soups" were formed. The complexes have been characterized by elemental analyses and by infrared, Raman, and pmr spectroscopy as well as by chemical reactions. Mechanistic implications are presented and discussed in relation to similar reactions with the analogous zerovalent platinum complexes. The relationships of these reactions to homogeneous catalysis by zerovalent complexes of the nickel triad are presented.

Introduction

The reactions of zerovalent palladium and platinum complexes have been related to the phenomena of chemisorption and a strong correspondence exists between the homogeneous catalytic reactions of these systems and heterogeneous catalysis by the metals themselves.³⁻⁵ Complexes of the types $M(PR_3)_4$ and $M(PR_3)_2(C_2H_4)$ ($M = Pd, Pt$) have been shown to undergo a wide variety of oxidative addition⁶⁻¹⁴ and ligand substitution reactions.¹⁴⁻²² Substitution reactions prevail for platinum and oxidative addition reactions for the palladium system. We have previously reported²³ that $Pt(PPh_3)_4$ reacts with terminal α -hydroxyacetylenes to yield two types of complexes (I and II).

A number of other workers have also investigated the reactions of platinum complexes with acetylenes.²⁴⁻²⁷ In con-



trast to the many detailed studies involving platinum, relatively few studies have been conducted with palladium.^{7,15,24-30}

It has been found that acetylenes react with complexes of the nickel triad to produce a wide variety of products among which are acetylene complexes as well as dimerization, trimerization, and polymerization products of the acetylenes themselves.²⁸⁻³⁴ The factors which seem to determine the nature of the products formed²⁸⁻³⁴ include the metal, its oxidation state, the nature of the acetylene, and the nature of other ligands coordinated to the metal. These reactions provide synthetically useful routes to organic compounds and metal complexes which in many cases are difficult if not impossible to prepare otherwise.²⁸⁻³⁴

Complex II seems to be unique among complexes of the nickel triad and few palladium hydrides are known.³⁵ However, both acetylide and acetylide hydride complexes have been implicated as catalysts in varied polymerization processes.²⁸⁻³⁴ Our continuing interest in acetylene complexes^{36,37} led us to undertake a study of the reactions of zerovalent palladium complexes with α -hydroxyacetylenes and other nonterminal and terminal acetylenes. The results of this study are reported herein.

Experimental Section

A. Reagents and Physical Measurements. The acetylenes phen-

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ylacetylene (Farchan), 2-butyne (Farchan), 1-ethynylcyclopentanol (Farchan), 1-ethynylcyclohexanol (Baker, Aldrich, and MCB), 3-methylbutyn-3-ol (Baker and Aldrich), 3-methyl-1-pentyn-3-ol (K&K), 1-propynylcyclohexanol (Farchan), propargyl alcohol (Aldrich), 2-methyl-3-pentyn-2-ol (Farchan), 1-propynylcyclopentanol (Farchan), and 1-phenyl-1-propyne (Farchan) were generally used without further purification. When purification was deemed necessary, it was accomplished by vacuum distillation. All boiling points agreed with the literature values.^{38,39} 1-Ethynylcycloheptanol was prepared from cycloheptanone by the literature method.⁴⁰ 1,1-Diphenyl-2-propyn-1-ol was prepared from benzophenone⁴¹ and lithium acetylide-ethylene-diamine (Foote Chemical). An adaptation of the method of Dominguez and Garza⁴⁰ was used to prepare 2-phenyl-3-butyne-2-ol from acetophenone in 75% yield (bp 66–68° (0.1 mm)).

The deuterated acetylene 3-methyl-1-butyne-3-ol-1, $O-d_2$ was prepared as follows. To 110 g of calcium carbide suspended in 30 ml of tetrahydrofuran (freshly distilled from calcium hydride), as a moderator, was added 50 ml of deuterium oxide dropwise with stirring. After passing through a column containing calcium carbide as a drying agent, the evolved dideuterioacetylene (in tenfold excess) was passed into dry tetrahydrofuran (250 ml) while ethylmagnesium bromide (0.3 mol in tetrahydrofuran) was also being added dropwise. After the addition of the Grignard was complete, dry acetone (22 ml) was added, and the solution heated to reflux for 3 hr. This entire procedure was performed under dry N_2 . The reaction was then quenched with 15 ml of a saturated solution of ammonium chloride in deuterium oxide. The tetrahydrofuran solution was separated and dried over sodium sulfate, the THF was removed on a rotary evaporator, and the residue was vacuum distilled to yield 5 g of pure product (nmr) (bp 99–100°; the nondeuterated analog boils at 104°).^{38,39}

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)palladium(0),^{42–44} *trans*-dichlorobis(triphenylphosphine)palladium(II),⁴⁵ ethylenebis(methyldiphenylphosphine)palladium(0),⁴⁶ ethylenebis(triphenylphosphine)palladium(0),⁴⁶ and bis(2,4-pentanedionato)palladium(II)⁴⁷ were prepared according to literature procedures.

Infrared spectra were recorded on Beckman IR-8 and IR-12 and Perkin-Elmer 621 and 221 recording spectrophotometers as KBr pellets (IR-8, IR-12, 221) or Nujol mulls between cesium bromide disks (621) for the complexes and as neat liquids for the acetylenes. The IR-8 spectra were calibrated with known frequency bands of polystyrene while spectra on the other instruments were calibrated using water vapor absorptions. The data are believed to be accurate to within $\pm 5 \text{ cm}^{-1}$. Proton nmr spectra were obtained on the Varian Associates A-60, HA-60-1L, T-60, and HA-100 and the Jeolco 4H-100 nmr spectrometers as deuteriochloroform solutions with tetramethylsilane as internal standard. The 4H-100, HA-100, and HA-60-1L spectrometers were calibrated by the frequency side-band technique. Laser Raman spectra were recorded on a Jarrell-Ash 25-500 spectrophotometer equipped with a Coherent Radiation Laboratories Model 52G mixed-gas laser. Melting points were determined in air on a Fischer-Johns melting point apparatus and are uncorrected. All samples melted with decomposition to red liquids. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. They are listed in Table I.

B. Preparation of the Complexes. Nearly all the complexes were prepared by four general methods. (See Table I.) An example of each method is given below.

1. *trans*-Bis(1-ethynylcyclopentanol)bis(triphenylphosphine)palladium(II). (a) **Method I.** To 0.25 g (2.17×10^{-4} mol) of freshly prepared $((C_6H_5)_3P)_4Pd$ suspended in 20 ml of dry benzene under nitrogen was added 0.11 g (1×10^{-3} mol) of 1-ethynylcyclopentanol

followed directly by 10 ml of methanol. The previously light yellow-brown benzene solution turned yellow-brown upon addition of the methanol. Reduction of the solution to near dryness under reduced pressure resulted in the deposition of small colorless crystals. These were recrystallized by dissolving in the minimum amount of dichloromethane, filtering to remove traces of palladium metal, and concentrating by aspiration to near dryness, followed by addition of anhydrous ethyl ether to incipient precipitation. The product was filtered, washed with 15 ml of anhydrous ethyl ether, and dried in a vacuum desiccator over P_4O_{10} : yield 0.085 g (46%); colorless crystals; dec pt 163–166°.

(b) **Method II.** To a suspension of 0.30 g (4.27×10^{-4} mol) of *trans*-dichlorobis(triphenylphosphine)palladium(II) and 0.35 g (1.34×10^{-3} mol) of triphenylphosphine in 50 ml of dry benzene was added a solution containing 0.22 g (1.6×10^{-3} mol) of 1-ethynylcyclopentanol in 15 ml of absolute ethanol. To this suspension was added with vigorous stirring 0.1 g (2.56×10^{-3} mol) of sodium borohydride in small pieces. Immediate effervescence occurred upon the addition of the sodium borohydride and the originally lemon yellow suspension gradually lightened in color. The solution was stirred open to the air until effervescence ceased and then stoppered and stirred for 48 hr. The white crystalline product which deposited from a colorless solution was filtered and washed with 50 ml of absolute ethanol and 50 ml of anhydrous ethyl ether. The ethanol-ether filtrate was discarded and the precipitate was washed with 75 ml of dichloromethane. The dichloromethane filtrate was concentrated nearly to dryness by aspiration and 30 ml of anhydrous ethyl ether added. The resultant colorless crystalline precipitate was filtered and washed with 30 ml of anhydrous ethyl ether. Recrystallization as in method I afforded 0.120 g (33.1%) of colorless crystals, dec pt 163–166°.

(c) **Method III.** To a solution containing 0.3 g (1×10^{-3} mol) of bis(2,4-pentanedionato)palladium(II), 1.3 g (5×10^{-3} mol) of triphenylphosphine, and 0.88 g (6.4×10^{-3} mol) of 1-ethynylcyclopentanol in 25 ml of dry benzene and 10 ml of absolute ethanol was added 0.32 g (8×10^{-3} mol) of sodium borohydride in small pieces. Upon the addition of the sodium borohydride to the light lemon yellow solution there was immediate effervescence and the solution gradually became colorless (*ca.* 24 hr) with the deposition of colorless crystals. These were isolated and recrystallized as in method I to yield 0.31 g (36.6%) of colorless crystals, dec pt 160–162°.

(d) **Method IV.** To 0.45 g (6.85×10^{-4} mol) of ethylenebis(triphenylphosphine)palladium(0) freshly prepared under nitrogen⁴⁶ and washed under nitrogen with 50 ml of anhydrous ethyl ether was added 25 ml of dry benzene, 5 ml of absolute ethanol, and 2.266 g (2.06×10^{-2} mol) of 1-ethynylcyclopentanol at 0°. The resulting deep red solution was flushed with nitrogen and allowed to attain room temperature slowly under nitrogen. After 24 hr the solution was nearly colorless and contained small colorless crystals. The solution was then filtered and the crystalline product was washed with 10 ml of absolute ethanol and 50 ml of anhydrous ether. Recrystallization as in method I afforded 0.35 g (60%) of colorless crystals, dec pt 160–163°.

2. *trans*-Bis(phenylacetylide)bis(methyldiphenylphosphine)palladium(II). To 0.50 g (9.4×10^{-4} mol) of ethylenebis(methyldiphenylphosphine)palladium(0), which had been washed with 50 ml of anhydrous ether under nitrogen and dissolved in 30 ml of dry benzene under nitrogen, was added 0.286 g (2.8×10^{-3} mol) of phenylacetylene. The initially light yellow solution turned blood red upon addition of the acetylene. The flask was stoppered tightly and refrigerated at 10° for 24 hr. After 24 hr colorless crystals had deposited from a red-orange solution. These were filtered, washed with 100 ml of anhydrous ether, and recrystallized from hot dichloromethane to yield 0.333 g (50%) of colorless crystals, dec pt 145–147°.

3. *trans*-Bis(triphenylphosphine)bis(1-ethynylcyclopentanol)platinum(II) and *trans*-Bis(triphenylphosphine)bis(1-ethynylcycloheptanol)platinum(II). These were prepared from tetrakis(triphenylphosphine)platinum(0)⁴⁸ and the appropriate acetylene in 50:50 ethanol-benzene in 50% yield by the same procedure described for complex II.²³

Results

The elemental analyses (Table I), infrared spectral data (Table II), and pmr data (Table III) indicate that the zero-valent palladium complexes $((C_6H_5)_3P)_nPd$ ($n = 3$ or 4), $((C_6H_5)_3P)_2Pd(C_2H_4)$, and $((CH_3)_2PC_6H_5)_2Pd(C_2H_4)$ react with terminal acetylenes to produce the stable palladium(II)-bis(acetylide) complexes $(R_3P)_2Pd(C\equiv CR)_2$ having a *trans*

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Table I. Elemental Analyses and Physical Properties

Complex	Mp, ^a °C	% carbon		% hydrogen		% phosphorus		Prepn method
		Calcd	Found	Calcd	Found	Calcd	Found	
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{C}_5\text{H}_9\text{OH} \end{array} \right)_2$	163-166	70.05	69.96	5.87	5.75	7.26	7.09	I-IV
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{C}_6\text{H}_{11}\text{OH} \end{array} \right)_2$	155-157	71.0	71.20	6.18	6.03	7.05	6.98	I-IV
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{C}_7\text{H}_{13}\text{OH} \end{array} \right)_2$	126-128	71.5	71.72	6.40	6.45	6.84	7.29	I-III
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} C_6H_5 \\ \\ \text{C}\equiv\text{C} \\ \\ OH \end{array} \right)_2$	161-164	75.8	75.69	5.16	5.04	5.92	5.75	I-III
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} CH_3 \\ \\ \text{C}\equiv\text{C} \\ \\ OH \end{array} \right)_2$	144-146	69.2	69.4	5.76	5.62	7.75	7.76	I-IV
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} CH_3 \\ \\ \text{C}\equiv\text{C} \\ \\ OH \end{array} \right)_2^b$	143-144	69.2	69.27	5.76	5.41	7.75	7.69	II
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} C_2H_5 \\ \\ \text{C}\equiv\text{C} \\ \\ OH \end{array} \right)_2$	147-149	69.6	69.23	6.05	6.01	7.49	7.55	I-IV
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} C_6H_5 \\ \\ \text{C}\equiv\text{C} \\ \\ OH \end{array} \right)_2$	148-150	72.9	73.01	5.45	5.33	6.70	6.63	I-III
$((C_6H_5)_3P)_2Pd(C\equiv CC_2H_5)_2^c$	145-147	74.85	75.07	5.03	5.24	7.43	7.38	I-IV
$((CH_3)_2PC_6H_5)_2Pd(C\equiv CC_6H_5)_2$	137-141	65.7	65.8	5.4	5.31	10.6	10.68	IV
$((C_6H_5)_3P)_2Pt \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{C}_5\text{H}_9\text{OH} \end{array} \right)_2$	250-252	64.5	63.56	5.36	5.24	6.58	6.75	<i>d</i>
$((C_6H_5)_3P)_2Pt \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{C}_7\text{H}_{13}\text{OH} \end{array} \right)_2$	218-222	64.8	65.14	5.85	5.41	6.2	6.75	<i>d</i>

^a All complexes melted with decomposition to red liquids. ^b Prepared from Pd(PPh₃)₂Cl₂, PPh₃, DC≡CC(CH₃)₂OD, and NaBD₄ in THF, as in method II. ^c Per cent palladium: calcd, 12.70; found, 12.50. ^d Prepared by method I from Pt(PPh₃)₄. See ref 23.

square-planar configuration. This is in marked contrast to the results of similar reactions of terminal acetylenes with zerovalent platinum complexes.²³⁻²⁷

The infrared and Raman spectra of the palladium complexes show a single slightly asymmetric band in the vicinity of 2100 cm⁻¹ attributable to ν_{C≡C}. This band is more intense in the Raman spectra than in the infrared spectra. The band is only very slightly decreased in intensity when the complex is prepared from a deuterated acetylene and no splitting of this band was observed for any of the samples in a large number of spectra obtained on several different spectrometers by three separate investigators. When type II acetylene com-

plexes of platinum are prepared from deuterated acetylenes, this band is considerably decreased in intensity²³ suggesting that for these complexes it is composed of two overlapping bands, ν_{C≡C} and ν_{Pt-H}, with the predominant intensity arising from ν_{Pt-H}. In addition, a single band in the region 530-565 cm⁻¹ attributable⁴⁹ to ν_{Pd-C} was observed for all complexes where other vibrations did not interfere. If the complexes possessed a cis configuration and C_{2v} symmetry, two absorptions should be observed for both ν_{C≡C} and ν_{M-C} with

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Table II. Infrared Spectral Data for the Complexes (cm^{-1}) (KBr Pellets)

Complex	$\nu_{\text{C}\equiv\text{C}}$ (complex)	$\nu_{\text{C}\equiv\text{C}}$ (free)	ν_{OH} (complex)	$\Delta\nu_{\text{OH}}$	$\nu_{\text{M}-\text{C}}$ (complex)
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{OH} \end{array} \begin{array}{c} \text{Cyclopentane ring} \end{array} \right)_2$	2117	2120	3423	-197	539
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{OH} \end{array} \begin{array}{c} \text{Cyclohexane ring} \end{array} \right)_2$	2109	2117	3493	-123	535
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{OH} \end{array} \begin{array}{c} \text{Cycloheptane ring} \end{array} \right)_2$	2121	2120	3423	-27	538
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}\equiv\text{CC} \\ \\ \text{OH} \end{array} \text{C}_6\text{H}_5 \right)_2$	2113	2118	3436	-104	565
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C}\equiv\text{CC} \\ \\ \text{OH} \end{array} \text{CH}_3 \right)_2$	2109	2114	3520	-100	530
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{C}\equiv\text{CC} \\ \\ \text{OH} \end{array} \text{CH}_3 \right)_2^a$	2109 1530	2114	3525	-95	
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}\equiv\text{CC} \\ \\ \text{OH} \end{array} \text{CH}_3 \right)_2$	2109	2125	3520	70	
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd} \left(\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}\equiv\text{CC} \\ \\ \text{OH} \end{array} \text{CH}_3 \right)_2$	2105	2103	3545	-50	
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}\equiv\text{CC}_6\text{H}_5)_2^b$	2110	2109			548
$((\text{CH}_3)_2\text{PC}_6\text{H}_5)_2\text{Pd}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$	2110	2109			
$((\text{C}_6\text{H}_5)_3\text{Pt} \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{OH} \end{array} \begin{array}{c} \text{Cyclopentane ring} \end{array} \right)_2$	2109	2120	3620	-280	
$((\text{C}_6\text{H}_5)_3\text{Pt} \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{OH} \end{array} \begin{array}{c} \text{Cycloheptane ring} \end{array} \right)_2$	2105	2121	3373	-67	
$((\text{C}_6\text{H}_5)_3\text{Pt} \left(\begin{array}{c} \text{C}\equiv\text{C} \\ \\ \text{OH} \end{array} \begin{array}{c} \text{Cyclohexane ring} \end{array} \right)_2 (\text{H})_2$	2120	2117	3620	0	

^a Prepared from deuterated acetylene. ^b Masai, *et al.*,⁴⁹ reported $\nu_{\text{C}\equiv\text{C}}$ at 2110 cm^{-1} and $\nu_{\text{M}-\text{C}}$ at 548 cm^{-1} .

only one band coincident in the Raman and infrared spectra. These results are only consistent with D_{2h} symmetry and a trans configuration about the palladium.

The OH stretching frequency, ν_{OH} , for the palladium acetylides is shifted to lower energy by about 100 cm^{-1} (50 to 197 cm^{-1}) relative to that of the free acetylene for all complexes except $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}\equiv\text{CC}(\text{OH})(\text{CH}_3)_2)_2$ where it is shifted to higher energy by 70 cm^{-1} . Chatt,⁵⁰ *et al.*,

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

found that for μ -bonded platinum(II)-dihydroxyacetylene complexes of the type $\text{K}[\text{PtCl}_3\text{RC}_2\text{R}]$, ν_{OH} shifted to lower energy by 110 – 140 cm^{-1} . We²³ previously reported that for μ -bonded platinum(0)- α -hydroxyacetylene complexes (type I) ν_{OH} shifted to lower energy by 45 – 260 cm^{-1} but that ν_{OH} did not shift at all for σ -bonded platinum(IV) acetylide hydrides (type II). These results are consistent with metal-OH interactions in all but type II complexes where no vacant coordination sites are available for this type of interaction.

Chatt,⁵⁰ *et al.*, found that the proton resonance of the hy-

Table III. Nmr Spectral Data for the Complexes

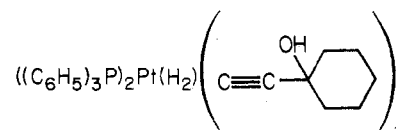
Complex	$\tau,^a$ ppm			
	C_6H_5	CH_3	CH_2	OH
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - \text{Cyclopentane} \end{array} \right)_2$	2.2 m 2.6 m		8.76 m	8.42 s
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - \text{Cyclohexane} \end{array} \right)_2$	2.20 m 2.62 m		9.0 m	9.35 s
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - \text{Cycloheptane} \end{array} \right)_2$	2.20 m 2.62 m		8.83 m	9.38 s
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - C_6H_5 \\ \\ C_6H_5 \end{array} \right)_2$	2.25 m 2.62 m 2.96 s			8.45 s
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - CH_3 \\ \\ CH_3 \end{array} \right)_2$	2.35 m 2.53 m	9.2 s		9.32 s
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - C_6H_5 \\ \\ CH_3 \end{array} \right)_2$	2.25 m 2.70 m 2.97 m	9.0 s		9.10 s
$((C_6H_5)_3P)_2Pd \left(\begin{array}{c} OH \\ \\ C \equiv C - C_6H_5 \\ \\ CH_3 \end{array} \right)_2$	2.2 m 2.6 m	9.25 s 9.51 ^b t	9.11 ^b q	9.4 s
$((C_6H_5)_3P)_2Pd(C \equiv CC_6H_5)_2$	2.15 s 2.65 m			
$((CH_3)_2PC_6H_5)_2Pd(C \equiv CC_6H_5)_2$	2.1 m 2.58 m 2.8 s	8.0 ^c t		
$((C_6H_5)_3P)_2Pt \left(\begin{array}{c} OH \\ \\ C \equiv C - \text{Cyclopentane} \end{array} \right)_2$	2.25 m 2.65 m		8.73 m	9.42 s
$((C_6H_5)_3P)_2Pt \left(\begin{array}{c} OH \\ \\ C \equiv C - \text{Cyclohexane} \end{array} \right)_2$	2.26 m 2.66 m		8.83 m	Obscured

^a Key: m, multiplet; s, singlet; t, triplet; q, quartet. ^b ³J_{H-H} = 6.5 Hz. ^c |²J_{H-H} + ⁴J_{H-H}| = 3.6 Hz.

droxyl proton of $K[PtCl_3RC_2R]$ shifted downfield by 1.5 τ units whereas we²³ observed an upfield shift in the OH resonance for $(R_3P)_2Pt(RC \equiv CR)$. An even greater upfield shift in this resonance for $trans-(R_3P)_2M(C \equiv CR)_2$, where M = Pd or Pt, is observed here. Apparently, palladium(II) and platinum(II) interact with the hydroxyl group to a greater extent than platinum(0). This interaction does not seem to provide either a stabilizing interaction or a rate enhancement for the production of these complexes as complexes prepared from phenylacetylene appear to be just as stable and form just as rapidly.

The pmr spectra of the complexes $(R_3P)_2M(C \equiv CR)_2$ (M = Pd, Pt) have the following general features: two unresolved

multiplets (Figure 1) centered at *ca.* τ 2.2 and 2.6 (phenyls), a singlet in the range τ 8.42–9.42 (OH), and methylene and methyl resonances both of which are shifted to slightly higher field compared to the free ligand. The resolution of the phenyl resonances into two broad multiplets is both striking and informative. Figure 1 shows it is distinctly different from $(Ph_3P)_2PtHC \equiv CC(CH_3)_2OH$ or other type I complexes where the two phosphines possess a *cis* relationship. This same phenomenon occurs with a wide variety of complexes possessing phenyl groups attached to phosphorus where the geometry can be ascertained *via* an independent indicator.⁵¹ Seemingly when phenylphosphines are *trans* to one another the phenyl resonance occurs as two broad multiplets, whereas when these phosphines are *cis*, only one broad multiplet is generally observed. The difference can most likely be attributed to differences in the magnitude of ²J_{P-P} where this is much greater⁵² for mutually *trans* phosphines than for mutually *cis* phosphines. The *trans* geometry in these complexes is further supported by the observation that the phosphine methyl resonance for the complex $((CH_3)_2PC_6H_5)_2Pd(C \equiv CC_6H_5)_2$ appears as a triplet^{51–55} due to "virtual coupling." In addition, X-ray crystallographic and neutron diffraction data⁵⁶ for the complex



indicate that this complex crystallizes as monoclinic crystals of space group $P2_1/c$ with the platinum centrosymmetrically surrounded by a coplanar arrangement of two phosphorus and two carbon atoms. The hydride hydrogens have not yet been definitively located.

The efforts of three different investigators on as many different instruments showed no evidence for a high-field metal hydride resonance in the region τ 10–40 for any of the complexes reported in this work including the two platinum complexes analogous to complex II. This result coupled with the vibrational spectroscopy results (*vide supra*) leads us to conclude that these complexes are indeed not the anticipated hydrides but rather *trans* square-planar bis(acetylide)bis(phosphine)palladium(II) complexes.

The complexes have been further characterized by chemical reactions. None of the complexes showed any evidence of the production of dichloromethane upon prolonged storage in chloroform solution nor did they react with carbon tetrachloride to produce chloroform, reactions typical of transition metal hydrides³⁵ including complex II.²⁵ They did, however, undergo some form of decomposition as evidenced by the formation of dark viscous solutions. The complex *trans*- $((C_6H_5)_3P)_2Pd(C \equiv CC_6H_5)_2$ reacted with HCl in benzene to produce *trans*- $((C_6H_5)_3P)_2PdCl_2$ and phenylacetylene nearly quantitatively. *trans*- $((C_6H_5)_3P)_2PdCl_2$ was identified by melting point and pmr and infrared spectroscopy, while the phenylacetylene was identified by boiling point and pmr and infrared spectroscopy.

Several of the complexes were allowed to react with car-

- (51) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).
- (52) W. McFarlane, *J. Chem. Soc. A*, 1922 (1967).
- (53) J. G. Verkade, R. P. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).
- (54) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).
- (55) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
- (56) S. E. Rasmussen, private communication, Department of Inorganic Chemistry, Aarhus University, Aarhus, Denmark.

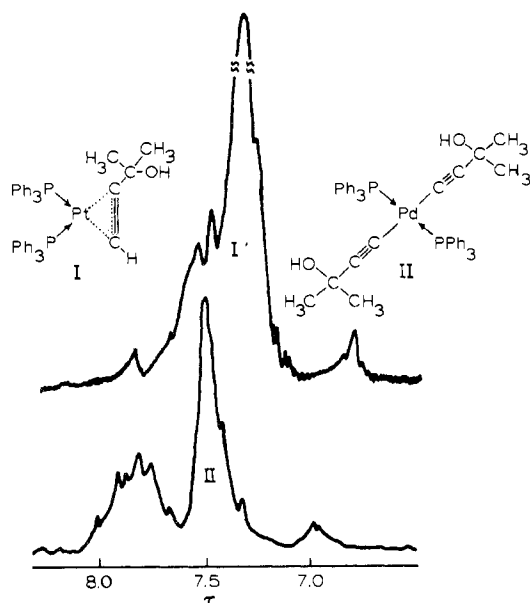


Figure 1. Pmr spectra in the phenyl region for complexes I and II, as deuteriochloroform solutions obtained on a Varian A-60 spectrometer.

bon monoxide at room and elevated temperatures and at atmospheric and elevated pressures. In all cases a deep red solution was formed whose infrared spectrum suggested the presence of $(\text{Ph}_3\text{P})_3\text{PdCO}$ ⁵⁷ as evidenced by $\nu_{\text{C}\equiv\text{O}}$ at 1950 cm^{-1} in benzene solution. The red solutions ultimately deposited black tars and elemental palladium and $(\text{Ph}_3\text{P})_3\text{PdCO}$ could not be isolated from any of these reactions.

Discussion

Although the preparations of each of these complexes have been repeated numerous times by three of the authors, only about 60% of the attempts were met with successful isolation of the desired complex. The absence or presence of air, moisture, or light, temperature of the solvent, and time are not critical factors. Protonic solvents seem to be necessary as reactions in benzene or tetrahydrofuran alone seldom led to the production of the complexes whereas either solvent with ethanol, water, or acetic acid added usually did, a trace of acetic acid being the most effective.

One recurring difficulty was the production of as yet uncharacterized black tars or "thick black soups." This was aggravated by the presence of a large excess of the acetylene and is probably due to palladium-catalyzed acetylene polymerization or oligomerization. Borate esters rather than complexes were often produced; an excess of sodium borohydride aggravated this.

The stability of the complexes is also quite variable; different samples of the same substance in the solid state have lasted for periods as short as 24 hr to over 2 years without decomposition. Neither the method of storage of the solid nor the method of preparation has an apparent effect upon stability. Purity however seems to be a determining criterion as samples containing trace amounts of excess acetylene or halocarbons decompose to black tars within hours. Chloroform or benzene solutions of the complexes also lead to decomposition, with chloroform the more rapid. The complexes have much greater kinetic stability in dichloromethane than in chloroform, allowing recrystallization from dichloromethane but not from chloroform.

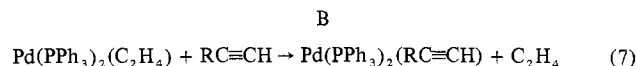
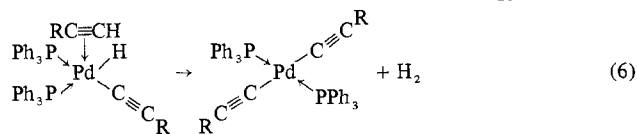
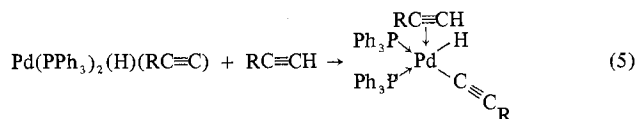
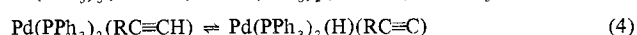
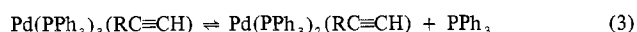
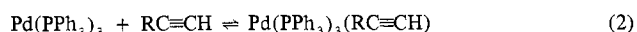
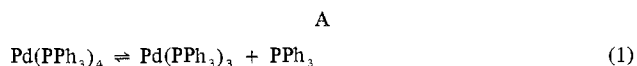
(57) A. Misono, Y. Uchida, M. Hidai, and K. Kudo, *J. Organometal. Chem.*, **20**, P7 (1969).

Most of the complexes have been prepared by at least three of the four general preparative methods described, with method II generally the most successful. The darker the solutions became during the preparative reactions, the smaller the yield. Any of these acetylenes could be added to a solution of any of their complexes in nearly any solvent in which the complex will dissolve with the subsequent formation of "thick black soups." In reactions with nonterminal acetylenes "thick black soups" or gummy tars were always formed instead of complexes. Maitlis, *et al.*,²⁶ have previously noted similar results with nonterminal alkyl- and arylacetylenes. This makes it tempting to suggest that these complexes are, in fact, active intermediates in the polymerization of acetylenes.⁵⁸

Although several monohydrides³⁵ and dihydrides^{23,35} of platinum phosphines have been prepared, characterized, and studied, as might be anticipated, few palladium phosphine hydrides^{35,59} have been reported. All the palladium hydrides exhibit much lower thermal and aerobic stabilities than their platinum analogs. The chemical similarities of palladium and platinum⁵⁹ and their oxidation trends suggest that palladium-(IV) hydride complexes analogous to the platinum compound of type II might have been expected. However, the stabilities of starting materials,³⁻¹⁷ the reactions of known palladium hydrides,^{35,59} all the spectral evidence, and the chemical reactions of the complexes discussed above mitigate against this expectation.

The proposed mechanisms for these reactions are presented in Scheme I. In the absence of acetylene^{3,5,6,15,24,26} and the

Scheme I. Proposed Mechanism for the Reaction of Zerovalent Palladium-Phosphine Complexes with Terminal Acetylenes



presence of excess phosphine, preparative methods I-III lead only to $\text{Pd}(\text{PPh}_3)_4$. The dissociation of $\text{M}(\text{R}_3\text{P})_4$, where $\text{M} = \text{Ni}, \text{Pd},$ and Pt , to at least a three-coordinate species is known to occur.^{3,60-62} An X-ray structure analysis of $\text{Pt}(\text{PPh}_3)_3$ has shown it to have a trigonal-planar structure,⁶³ and such a

(58) It has been shown that analogous platinum complexes are indeed effective catalysts for the linear polymerization of acetylenes. See ref 33.

(59) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. I, Academic Press, New York, N. Y., 1971, pp 103-104.

(60) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

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

(62) W. C. Siedel and C. A. Tolman, *Inorg. Chem.*, **9**, 2354 (1970).

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

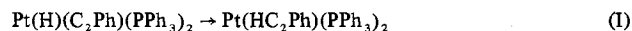
trigonal-planar structure would also be expected for $(\text{Ph}_3\text{P})_3\text{-Pd}$.⁴⁴ The lack of reactivity of $(\text{Ph}_3\text{P})_4\text{Pd}$ ⁶⁴ and the coordinative unsaturation of $(\text{PPh}_3)_3\text{Pd}$ allow the latter to coordinate easily with an acetylene to form $(\text{PPh}_3)_3\text{Pd}(\text{RC}\equiv\text{CH})$ (reaction 2). At least one example of a similar nickel complex⁶⁵ $\text{Ni}(t\text{-BuNC})_3(\text{TCNE})$ is known, formed from an equilibrium reaction of the three-coordinate complex and *tert*-butyl isocyanide in a reaction analogous to reaction 3.

For reactions involving the starting material $\text{Pd}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ reaction 7 would be the first reaction in the sequence. This complex is known to dissociate,^{46,65,66} and the analogous ethylene complexes of both nickel and platinum react with acetylenes to produce the zerovalent acetylene complexes¹⁵ $\text{M}(\text{PPh}_3)_2(\text{RC}\equiv\text{CR})$. In addition $\text{Pd}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ has been shown to react with acids to produce the hydrides⁴⁶ $\text{Pd}(\text{PPh}_3)_2\text{HX}$ by oxidative addition. Reaction 7 would be followed by reaction 4 since starting with reaction 4 the two mechanisms become the same.

Molecular orbital calculations⁶⁷⁻⁶⁹ have shown that when acetylenes become coordinated to transition metals, electron density is removed from the π orbitals of the acetylene moiety and shifted to its π^* orbitals. The formerly linear acetylenes thus become bent upon coordination (substantiated by X-ray crystallography¹⁵) and the two carbon atoms become electron rich and susceptible to electrophilic attack.¹⁵ This has been experimentally verified.⁷⁰

Calculations⁷¹ on complexes of the type $(\text{R}_3\text{P})_2\text{Pt}(\text{RC}\equiv\text{CH})$ indicate furthermore that they should be thermodynamically unstable with respect to the acetylidyde-hydride complexes $(\text{R}_3\text{P})_2\text{Pt}(\text{H})(\text{C}\equiv\text{CR})$. For $(\text{PH}_3)_2\text{Pt}(\text{CH}_3\text{C}\equiv\text{CH})$ and $(\text{PH}_3)_2\text{Pt}(\text{H})(\text{CH}_3\text{C}\equiv\text{C})$, respectively, the orbital energy sums are -650.35 and -653.36 eV and the overlap populations 6.31 and 6.60 with more negative orbital energy sum and more positive overlap population indicating greater stability. Since palladium and platinum have very similar⁷² first ionization potentials, these results should be valid for palladium as well.

In the analogous platinum system the following reaction has been shown to occur²⁴



and in most cases reactions of $\text{Pt}(\text{PPh}_3)_4$ with acetylenes lead to complexes of type I.^{5,26-30} However, we have isolated²³ one example of a type II complex as well as the two examples of $(\text{PPh}_3)_2\text{Pt}(\text{C}\equiv\text{CR})_2$ reported herein indicating

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(65) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 91, 6994 (1969).

(66) P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 10, 2210 (1971).

(67) K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 92, 5110 (1970).

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(70) See for example R. D. W. Kemmitt, B. Y. Kimura, and G. W. Littlecott, *J. Chem. Soc., Dalton Trans.*, 636 (1973); M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Amer. Chem. Soc.*, 95, 3030 (1973), and references contained therein.

(71) J. H. Nelson, K. S. Wheelock, J. D. Kelly, L. C. Cusachs, and H. B. Jonassen, *J. Chem. Soc., Dalton Trans.*, 1457 (1973).

(72) C. E. Moore, "Ionization Potentials and Ionization Limits Derived from Optical Spectra," NSRDS-NBS 34, National Bureau of Standards, Washington, D. C., 1970.

that $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_4$ probably react with acetylenes by similar mechanisms.

As early as 1948 Reppe and Schweckendieck⁷³ found that complexes of the type $\text{Ni}(\text{CO})_2(\text{R}_3\text{P})_2$ were active catalysts for the linear polymerization and cyclic trimerization of acetylenes. Meriwether and coworkers^{31,32,74,75} investigated the mechanisms of these polymerizations and found that the reactions were particularly effective with terminal acetylenes. Steric and electronic effects within the acetylene also markedly affected these reactions; compelling evidence for the participation of nickel hydrides in these reactions was also uncovered. Zerovalent complexes of the nickel triad, Ni, Pd, and Pt, might then all react with acetylenes *via* similar mechanisms, making these complexes the effective catalysts for acetylene polymerization. This in turn would then very probably make the complexes isolated here the active catalysts in such polymerizations.⁵⁸

The differences in the products isolated in the platinum and palladium systems are striking. For platinum a large number of zerovalent acetylene complexes of type II have been isolated,^{15,25-29} whereas for palladium these can only be isolated when the acetylene bears strong electron-withdrawing substituents.^{15,25-29} This suggests that even though the stability increases in the series¹⁵ $\text{Ni} < \text{Pd} < \text{Pt}$ for both $(\text{R}_3\text{P})_2\text{M}(\text{C}\equiv\text{CR})_2$ and $(\text{R}_3\text{P})_2\text{M}(\text{HC}\equiv\text{CR})$, the equilibrium in reaction 4 lies to the left for platinum and to the right for palladium. The palladium complexes will then probably prove to be the most effective catalytic system for the polymerization of acetylenes among the members of the nickel triad. Further work on the characterization of the "thick black soups" and the establishment of the reaction mechanism is currently in progress.

Acknowledgment. We thank Dr. M. Gordon and Dr. L. C. Cusachs for helpful and stimulating discussions, Mr. Gordon Boudreaux, Mr. Don Moore, Dr. J. J. R. Reed, and Dr. D. M. Roundhill for help with some of the pmr spectra, and Dr. F. G. Baglin for obtaining the laser Raman spectra. The financial assistance of the Esso Research Laboratories, Exxon Co., Baton Rouge, La., is gratefully acknowledged. J. H. Nelson wishes to acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Advisory Board of the University of Nevada-Reno.

Registry No. $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_7\text{H}_9\text{O})_2$, 42230-21-7; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{-Pd}(\text{C}_8\text{H}_{11}\text{O})_2$, 42230-22-8; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_9\text{H}_{13}\text{O})_2$, 42230-23-9; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_{11}\text{H}_{15}\text{O})_2$, 42230-24-0; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_5\text{H}_9\text{O})_2$, 42230-25-1; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_6\text{H}_9\text{O})_2$, 42230-26-2; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_{10}\text{H}_9\text{O})_2$, 42230-27-3; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pd}(\text{C}_8\text{H}_9)_2$, 31387-03-8; $((\text{CH}_3)_2\text{P}(\text{C}_6\text{H}_5)_2\text{Pd}(\text{C}_8\text{H}_9)_2$, 42230-29-5; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pt}(\text{C}_7\text{H}_9\text{O})_2$, 42230-30-8; $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Pt}(\text{C}_8\text{H}_{11}\text{O})_2$, 42230-31-9; $((\text{C}_6\text{H}_5)_3\text{P})_4\text{Pd}$, 14221-01-3; *trans*-dichlorobis(triphenylphosphine)palladium(II), 28966-81-6; bis(2,4-pentanedionato)palladium(II), 14024-61-4; ethylenebis(triphenylphosphine)palladium(0), 33395-22-1; ethylenebis(methyldiphenylphosphine)palladium(0), 42230-32-0; tetrakis(triphenylphosphine)platinum(0), 14221-02-4.

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