

PLATINUM-ACETYLENE COMPLEXES III. IMPLICATIONS OF HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA

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SUMMARY

High resolution PMR spectra were recorded on ten zerovalent platinum complexes of terminal acetylenic alcohols and methylacetylenic alcohols. The results indicate that the complexes are essentially planar in solution, that the methylacetylenic alcohol complexes dissociate and that these complexes undergo oxidative addition reactions with the solvent (CDCl_3).

INTRODUCTION

In an earlier publication the preparation and characterization of several platinum acetylene complexes were reported¹. One important and interesting part of this work was the proton NMR spectra of the complexes wherein the chemical shift of the complexed acetylenic hydrogen showed it to be in the region where olefinic protons are normally found. We interpreted this resonance on the basis of 60 MHz spectra as the X part of an AA'MX multiplet; this is borne out by the 100 MHz spectra. However, only four lines of the anticipated twelve line spectrum were observed at the lower resolution; therefore new coupling constants were determined. In addition to the previously reported complexes we have prepared complexes of methyl acetylenic alcohols for comparison.

EXPERIMENTAL

The compounds 2-methyl-3-pentyne-2-ol and 1-propynylcyclohexanol obtained from Farchan Research Laboratories were used without further purifications. The acetylenes 1,1-diphenyl-2-butyne-1-ol² and 1-propynyl-3,3,5,5-tetramethylcy-

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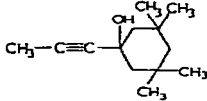
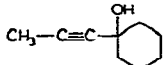
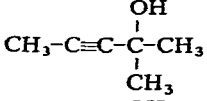
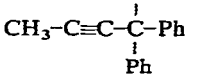
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clohexanol were prepared from the appropriate ketone and propynyllithium (Foote Chemical Company). The method used for preparing complexes has been previously reported¹. The new complexes were characterized by IR, PMR and elemental analyses (Tables 1 and 2). The 100 MHz PMR spectra were obtained with a Varian Associates HA-100 spectrometer operated in the field sweep mode and calibrated by the audio oscillation side band technique. The samples for NMR were dissolved in N₂ degassed CDCl₃ under nitrogen, filtered through glass wool into the NMR tubes, purged with nitrogen and sealed. The chemical shifts and coupling constants are recorded in Table 2.

TABLE 1

ELEMENTAL ANALYSES AND PHYSICAL PROPERTIES OF THE COMPLEXES (Ph₃P)₂Pt(acetylene)

Acetylene	$\nu(\text{C}\equiv\text{C})$ (cm ⁻¹)	$\Delta\nu(\text{C}\equiv\text{C})$ (cm ⁻¹)	M.p. ^a (°C)	Analysis found (calcd.) (%)		
				C	H	P
	1789	446	145-147	64.25 (64.50)	5.82 (5.70)	6.90 (6.77)
	1782	452	146-147	63.89 (63.50)	5.00 (5.10)	^b
	1799	421	138-141	61.65 (61.67)	4.95 (4.93)	7.75 (7.57)
	1799	458	160-161	66.28 (66.20)	4.72 (4.67)	6.69 (6.57)

^a All complexes melted with decomposition to red liquids. ^b Found: Pt, 22.28. Calcd.: Pt, 22.42%.

RESULTS AND DISCUSSION

Many complexes of the type (R₃P)₂M(Un); M = Ni, Pd, Pt and Un is an olefin or acetylene, have been prepared and characterized and the bonding in these complexes has led to much discussion³⁻⁹. The NMR spectra of these complexes have been particularly useful in the structural assignment due to the presence of ¹⁹⁵Pt (*I* = 1/2, 34% natural abundance) coupling in both the proton and fluorine NMR. The coupling constants *J* and chemical shifts τ of the various nuclei are such that many of the spectra can be interpreted by simple first order analyses. However, only two reports of 100 MHz PMR spectra for complexes of this type have appeared^{5,10}.

The chemical shift and coupling constant data for the complexes is given in Table 2. A typical spectrum is shown in Fig. 1. The conclusions which can be drawn from these spectra are the following: The chemical shift values of the acetylenic protons (Table 2) demonstrate that the complexed acetylene is spectroscopically equivalent to an olefin as its proton appears in the region where olefinic protons are

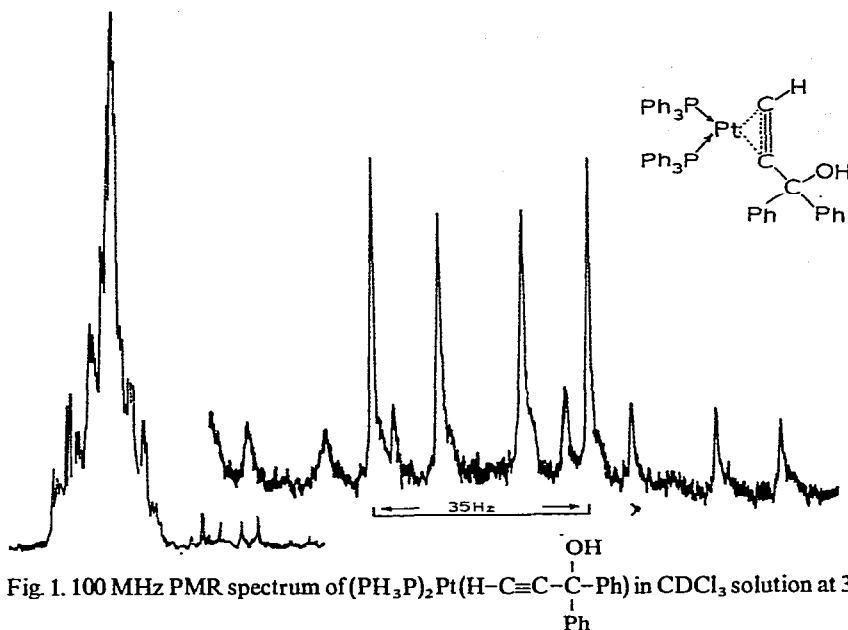


Fig. 1. 100 MHz PMR spectrum of $(\text{PH}_3\text{P})_2\text{Pt}(\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{Ph})\text{OH})$ in CDCl_3 solution at 32° . The inset is the expanded acetylene hydrogen $\text{C}\equiv\text{C}-\text{H}$ resonance showing the $\text{AA}'\text{MX}$ multiplet. The large resonance is the unresolved multiplet of the phenyl groups.

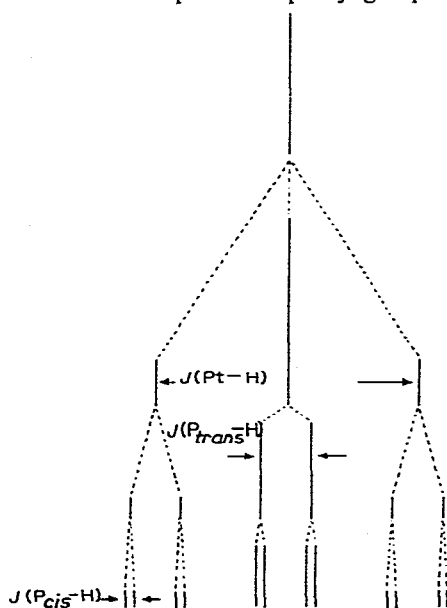
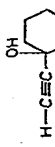
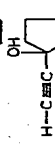

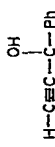

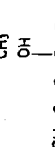
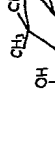


Fig. 2. Representation of the coupling for $\text{C}\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}-\text{CH}_3$ protons of platinum complexes of the type $(\text{PPh}_3)_2\text{Pt}(\text{R}-\text{C}\equiv\text{C}-\text{H})$ and $(\text{PPh}_3)_2\text{Pt}(\text{R}-\text{C}\equiv\text{C}-\text{CH}_3)$.

normally found¹². This is in agreement with the spectral shifts observed in the infrared and the lengthening of the $\text{C}-\text{C}$ bond determined by X-ray structure measurements¹³. Recently¹¹ it was shown by 60 MHz PMR studies on the complex $(\text{PPh}_3)_2\text{Pt}(\text{H}-\text{C}-$

TABLE 2.
100 MHz PMR DATA FOR SATURATED CDCl_3 SOLUTIONS OF COMPLEXES OF THE TYPE $(\text{Ph}_3\text{P})_2\text{Pt}(\text{acetylene})$
 τ values (ppm) relative to TMS internal standard

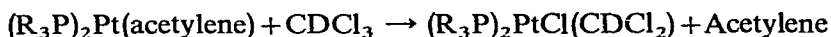
Acetylene	$\tau(\text{Ph})^a$	$\tau(\text{CH}_3)$	$\tau(\text{CH}_2)$	$\tau(\text{C}\equiv\text{C}-\text{H})$	$\tau(\text{OH})$	$J(\text{Pt}-\text{C}\equiv\text{C}-\text{H})$	$J(\text{Pt}-\text{C}\equiv\text{C}-\text{CH}_3)$	$J(\text{Pt}-\text{H})$	$J(\text{P}-\text{H})$
$\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{CH}_3)_2$	2.70	8.68 ^b	3.76	8.34 ^f	59.5	10	22		
	2.68	8.50 ^a	3.74	8.75 ^g	63	10	22.75		
	2.70	8.32 ^a	3.72	8.75 ^h	60	10	22		
	2.70	8.49 ^a	3.78	8.98 ⁱ	62	10	22		
$\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})-\text{C}_2\text{H}_5$	2.70	8.75 ^b 9.17 ^c	3.78	9.20 ^f	63.5	10.25	23.25		
	2.80		3.55	8.80 ^j	58	10	22.25		
	2.75	8.09	8.60	9.09 ^k		38	8		
$\text{CH}_3-\text{C}\equiv\text{C}-\text{C}(\text{OH})-\text{CH}_3$	2.74	8.72 9.23 ^d		8.91 ^l		40.5	8		
	2.83	8.71		8.16 ^l		40	8		
	2.74	8.42 9.07 9.28	8.58 8.75 8.82	9.18 ^m		36	8		

^a Center of a broad unresolved multiplet. ^b $J(\text{Pt}-\text{CH}_3) = 6$ Hz. ^c $J(\text{Pt}-\text{H}) = 1.5$ Hz for the ethyl group methyl hydrogens. ^d $J(\text{Pt}-\text{CH}_3) = 4$ Hz. ^e $J(\text{Pt}-\text{CH}_2) = 3$ Hz. ^f $J(\text{Pt}-\text{OH}) = 4$ Hz. ^g $J(\text{Pt}-\text{OH}) = 6$ Hz. ^h $J(\text{Pt}-\text{OH}) = 8$ Hz. ⁱ $J(\text{Pt}-\text{OH}) = 9$ Hz.

$\equiv\text{C-H}$) that the acetylenic hydrogen resonances were obscured by the phenyl proton resonances and these authors used perdeuteriotriphenylphosphine in place of triphenylphosphine as a ligand because of this. This is not the case for complexes of terminal acetylenes as is shown by the fact that all twelve of the anticipated lines due to the $\text{C}\equiv\text{C-H}$ proton are clearly observed to the high field side of the phenyl resonances at 100 MHz for these complexes.

The coupling scheme for the acetylenic and methylacetylenic protons can be analyzed as follows: These protons are the X part of $\text{AA}'\text{MX}$ and $\text{AA}'\text{MX}_3$ multiplets respectively which should contain twelve lines as shown in Fig. 2. There are two satellite lines due to coupling with ^{195}Pt and one line due to the uncoupled resonance in the relative intensity ratio of 1/4/1. These three lines are then further split by the non-equivalent *cis*- and *trans*-phosphorus atoms to give an apparent triplet of double doublets or twelve lines with relative intensities 1,1,1,1,4,4,4,1,1,1,1. The complexes of this type which have been studied by X-ray have been found to be essentially planar in the solid state¹⁴⁻¹⁷. Recent molecular orbital calculations have shown that this is the energetically favored configuration^{7,8,18}. The observation of non-equivalent coupling^{5,10} to the *cis*- and *trans*-phosphorus atoms implies the same structure in solution as in the solid state. Distinctive *cis*- and *trans*-coupling to the phosphorus atoms also implies that the rate of rotation of the acetylene is very slow on the NMR time scale (with an upper limit of ca. 1.2 sec^{-1}) based on the magnitude of $J(\text{P-H})$. Furthermore, the phosphorus-phosphorus coupling should be and is very small.

The presence of free acetylene in solutions of the complex $(\text{Ph}_3\text{P})_2\text{Pt}[(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{C}-\text{CH}_3]$ further complicates the spectra. The observation of separate resonances due to free and complexed acetylene implies a slow rate of ligand displacement. Furthermore, the concentration of free acetylene increases with increasing temperature, demonstrating that the displacement is temperature dependent. The spectra indicate that the reaction is not a simple dissociation reaction as the spectrum of a sample after a temperature cycle does not appear the same as that of one before a temperature cycle. Rather, an irreversible oxidative addition reaction involving the solvent most likely has occurred⁵:



The complex $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{CHCl}_2)$ has been isolated and characterized⁵ from the reaction of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3)$ and it was clearly shown that the carbon-chlorine bond had been broken with concurrent formation of platinum-chlorine and platinum-carbon bonds. Such reactions are similar to those which the zerovalent complexes $\text{M}(\text{Ph}_3\text{P})_4$, ($\text{M} = \text{Pd}, \text{Pt}$) undergo with halocarbons^{13,19-22} and offer chemical evidence confirming that the complexes of the type $\text{M}(\text{R}_3\text{P})_2(\text{Un})$ are indeed zerovalent^{1,7,8}. The solutions of all the complexes of dialkylacetylenes contain free acetylene but the solutions of the monoalkyl complexes do not. This suggests that the monoalkylacetylene complexes are more stable toward oxidative addition. This is in line with the predictions of the molecular orbital bonding model^{8,13} as the monosubstituted acetylenes should be better π -acceptors than the disubstituted acetylenes.

The spectrum of the 1-propynyl-3,3,5,5-tetramethylcyclohexanol complex possesses separate resonances for the axial and equatorial methyls on the cyclohexane ring demonstrating that the ring is not inverting in this complex. This is to be expected from the size of the ring substituents. In addition to this, the presence of free acetylene

in solution makes it difficult to specifically assign the ring methylene resonances.

The magnitudes of the platinum hydrogen coupling constants are very similar to those observed for analogous systems¹³. It is of interest to note that $J(\text{Pt-H})$ of analogous olefin and acetylene complexes are very similar in magnitude with the acetylene complexes usually displaying very slightly larger couplings.

The results of the molecular orbital calculations on systems¹⁸ of the type described in this work suggested that it might be possible to observe rotation of the coordinated acetylene about the metal-acetylene bond in the NMR spectra as observed in divalent complexes²³⁻²⁹. No evidence was found for rotation in the temperature range -60° to $+60^\circ$ in CDCl_3 . However, since halocarbon solvents oxidatively add, the observation of this rotation in these solvents at elevated temperatures may be impossible. Nevertheless, it may be possible to observe rotation at elevated temperatures in nonreactive solvents and work is in progress to clarify this point.

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