Reactions of *trans*-[PtClH(PPh$_3$)$_2$] † with α-Hydroxyacetylenes

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In the reactions between tertiary acetylenic alcohols and *trans*-[PtClH(PPh$_3$)$_2$] no insertion reactions into the Pt–H bond occur. In the presence of primary alcohols, R″OH, monochlorobis(triphenylphosphine)platinum complexes of alkynyl ethers, [PtCl{C≡CCR(R′)(OR″)}(PPh$_3$)$_2$], are obtained. Secondary and tertiary alcohols promote an intramolecular dehydration reaction and complexes of alkenylalkynes are formed.

INSERTION reactions of acetylenes and olefins into Pt–H and Pt–C bonds have been the subject of intense study in recent years [1-3] in connection with their role in the hydrogenation and polymerization reactions of unsaturated molecules. We have found that isopropenylacetylene and phenylacetylene insert into the Pt–H bond of *trans*-[PtClH(PPh$_3$)$_2$] giving *trans*-[PtCl(CH$_2$=C–R)-(PPh$_3$)$_2$] complexes (R = C$_6$H$_5$ or CMe=CH$_2$).[4]

Analytical data and physical properties of complexes *trans*-[PtCl{C≡C–CR(R′)(OR″)}(PPh$_3$)$_2$]

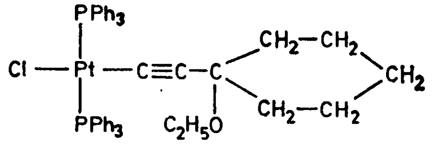
R	R′	R″	Analysis [a] (%) C	H	M.p. (θ_c/°C)	Yield (%)	I.r. (cm^{-1}) [b] ν(C≡C)	ν(C–O)	ν(Pt–Cl)	U.v. (nm) [c] max.	shoulder
Me	Me	Me	59.0 (59.2)	4.45 (4.60)	184—186	51	2 140	1 075	320	261 (4.54)	298 (3.74)
Me	Me	Et	59.75 (59.6)	4.55 (4.75)	184—185	62	2 130	1 070	320	261 (4.52)	296 (3.71)
Me	Me	Bu^n	60.3 (60.45)	4.80 (5.05)	200—202	30	2 140	1 080	320	260 (4.53)	295 (3.76)
Me	Me	CH$_2$CHMeCH$_2$Me	60.95 (60.8)	5.10 (5.20)	196—198	33	2 140	1 080	320	260 (4.51)	295 (3.73)
Me	Et	Me	59.25 (59.6)	4.70 (4.75)	185—187	51	2 140	1 080	320	260 (4.51)	297 (3.74)
Me	Et	Et	60.05 (60.0)	4.80 (4.95)	199—202	56	2 130	1 075	320	260 (4.51)	295 (3.72)
C$_5$H$_{10}$		Me	60.75 (60.55)	4.90 (4.85)	219—220	54	2 130	1 080	320	262 (4.51)	296 (3.70)
C$_5$H$_{10}$		Et	61.05 (60.95)	4.85 (5.00)	194—196	51	2 120	1 070	320	262 (4.51)	295 (3.79)

[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] Spectra in CHCl$_3$. Values of log ε are given in parentheses.

We have now extended our investigation to the reactions of *trans*-[PtClH(PPh$_3$)$_2$] with α-hydroxyacetylenes.

RESULTS AND DISCUSSION

We reported in a preliminary paper [5] that when 1-ethynylcyclohexan-1-ol is warmed with *trans*-[PtClH-(PPh$_3$)$_2$] in benzene, after addition of ethanol and standing overnight, a crystalline product separates. Its structure (see below) has been determined by *X*-ray analysis. During the course of the reaction, elimination of hydrogen and water occurs and no insertion products are obtained.



Analogous reactions take place with 2-methylbut-3-yn-2-ol and 3-methylpent-4-yn-3-ol giving monoalkynyl complexes of related ethyl ethers. Reaction carried out in CHCl$_3$ or in C$_2$H$_5$OH as solvents gave the same complexes in lower yields.

Analytical data of complexes are given in the Table. The i.r. spectra (Table) are characterized by a triple bond stretching band at 2 120—2 130 cm^{-1} and by a ν(Pt–Cl) band at 320 cm^{-1}. No bands are present in the region of OH stretching vibrations. A C–O stretching band of the ethereal bond at *ca.* 1 070 cm^{-1} confirms the occurrence of the etherification reaction. The u.v. spectra exhibit an inflection at *ca.* 295 nm and a maximum at 261 ± 1 nm. The spectra are similar to those of other monochloroplatinum acetylides previously synthesized.[6,7]

It was observed by Masai *et al.*,[8] who studied the u.v. spectra of some bis(acetylides) of nickel, palladium, and platinum, and by us in a recent investigation on a series of [Ni(NCS)(C≡CR)L$_2$] complexes (L = phosphine; R = aryl, alkenyl, or hydroxyalkyl),[9] that the first band is sensitive to conjugation and is shifted to lower wavelengths when saturated R radicals are present in alkynyl ligands. Thus in the spectra of the complexes in the Table the first band is observed as a shoulder, at *ca.* 295 nm, on the second band which is less sensitive to conjugation.

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† Chlorohydridobis(triphenylphosphine)platinum(II).

If other primary alcohols are used as precipitating agents the reactions follow an analogous pathway and complexes of the corresponding alkynyl ethers are obtained (Table). The spectral properties for all these complexes confirm structures analogous to the one determined by *X*-ray analysis[5] of *trans*-$[PtCl\{C{\equiv}C{-}C(C_5H_{10})OC_2H_5\}(PPh_3)_2]$ (Table).

The etherification reaction however does not occur by addition of secondary or tertiary alcohols. Reactions were carried out with 2-methylbut-3-yn-2-ol, 1-ethynylcyclohexan-1-ol, 3-methylpent-4-yn-3-ol, and t-butyl alcohol or isopropyl alcohol under the same conditions (see Experimental section). The crystalline products obtained were identified as the corresponding monochloroacetylides of the related alkenylalkynes, $[PtCl(C{\equiv}C{-}R)(PPh_3)_2]$ [R = $CMe{=}CH_2$, $CMe{=}CHMe$, or $\overline{C{=}CH(CH_2)_3CH_2}$], previously prepared by refluxing *cis*-$[PtCl_2(PPh_3)_2]$ and the same acetylenic alcohols for *ca.* 12 h in $CHCl_3$.[7] Secondary and tertiary alcohols promote an intramolecular dehydration reaction.

When 2-methylbut-3-yn-2-ol was warmed in the presence of *trans*-$[PtClH(PPh_3)_2]$ for a few minutes (without addition of solvents) the mixture rapidly became a brown colour. To avoid polymerization, warming was interrupted and the oily reaction mixture was cooled to 0 °C. By addition of CH_3OH, *trans*-$[PtCl(C{\equiv}C{-}CMe{=}CH_2)(PPh_3)_2]$[7] was obtained. An excess of 2-methylbut-3-yn-2-ol exerts the same influence on the reaction pathway as a tertiary alcohol and water is eliminated by an intramolecular dehydration reaction; 1-ethylnylcyclohexan-1-ol and 3-methylpent-4-yn-3-ol exhibit a similar behaviour.

When *trans*-$[PtClH(PPh_3)_2]$ reacts with acetylenic alcohols to give the monochloroacetylides, elimination of hydrogen occurs. Nuclear magnetic resonance spectra do not exhibit Pt–H resonances at high fields unlike the $[PtClH(PPh_3)_2]$ starting complex [τ(Pt–H) = 26.1.][10] or the other platinum hydride complexes such as *trans*-$[PtH_2(C{\equiv}C{-}R)_2(PPh_3)_2]$ ($R = C_6H_{10}OH$) [τ(Pt–H) = 22.88].[11]

We considered the hypothesis of hydrogen transfer to the excess of unsaturated ligand, but no reduction products were identified in the reaction mixtures by gas chromatographic analysis.

Conclusions.—The dehydration reactions of tertiary acetylenic alcohols, observed in the course of this investigation, probably occur because tertiary carbonium ions are formed in the intermediate stages of the reaction pathway.

Clark and co-workers[12-17] have studied extensively cationic acetylenic platinum complexes, in which platinum-induced carbonium ions are formed by delocalization of the positive charge of the complex over the coordinated acetylene molecule.

Cationic intermediates cannot always be isolated however, and our attempts at isolating cationic complexes in the course of these dehydration reactions by addition of $Ag[PF_6]$ or $[NH_4][PF_6]$ were unsuccessful.

Secondary acetylenic alcohols such as but-3-yn-2-ol or phenylprop-2-yn-1-ol or the primary acetylenic propargyl alcohol exhibit a different behaviour under similar reaction conditions and complex mixtures of products have been obtained. These reactions are the subjects of further investigation; in fact, as was observed by Clark and co-workers, the R substituents of the acetylene molecule strongly influence the course of the reaction between acetylenes and platinum complexes.

EXPERIMENTAL

Reagents and Apparatus.—2-Methylbut-3-yn-2-ol (Fluka), 1-ethynylcyclohexan-1-ol (Fluka), and 3-methylpent-4-yn-3-ol (Schuchardt) were used without further purification. Reagent grade solvents were used.

The complex *trans*-$[PtClH(PPh_3)_2]$ was prepared according to the method of Bailar and Itatani.[18]

Ultraviolet spectra were recorded on a Beckman DK 2A spectrophotometer and i.r. spectra were run on a Perkin-Elmer model 577 spectrophotometer as Nujol mulls.

Elemental analyses were carried out by Laboratorio di Microanalisi, Istituto di Chimica Farmaceutica, Pisa.

Reactions of Acetylenic Tertiary Alcohols with trans-$[PtClH(PPh_3)_2]$.—(a) *Addition of primary alcohols as precipitating agents.* The complex *trans*-$[PtClH(PPh_3)_2]$ (500 mg, 0.66 mmol) and benzene (10 cm^3) were warmed under reflux to obtain a clear solution. t-Acetylenic alcohol, $H{-}C{\equiv}C{-}R$ [$R = CMe_2OH$; $C(Me)(OH)C_2H_5$; $C_6H_{10}OH$] (*ca.* 10 mmol), was then added. The mixture was refluxed for *ca.* 30 min and, after cooling at room temperature, a primary alcohol (MeOH, EtOH, Bu^{n}OH, or $MeCH_2CHMeCH_2OH$) (25 cm^3) was added.

By cooling at 0 °C for *ca.* 24 h crystalline products were obtained, which were recrystallized from benzene–C_2H_5OH. Yields and melting points are given in the Table.

(b) *Reactions carried out in mass. Addition of* CH_3OH *as precipitating agent.* The complex *trans*-$[PtClH(PPh_3)_2]$ (500 mg) was added to the tertiary acetylenic alcohol $H{-}C{\equiv}C{-}R$ [$R = CMe_2OH$, $C(Me)(OH)C_2H_5$, or $C_6H_{10}OH$] (5 cm^3). The mixtures were warmed for a few minutes and then CH_3OH was added.

By cooling, complexes of the related alkenylalkynes, $[PtCl(C{\equiv}C{-}R)(PPh_3)_2]$ [R = $CMe{=}CH_2$, $CMe{=}CHMe$, or $\overline{C{=}CH(CH_2)_3CH_2}$], were obtained.

(c) *Addition of secondary or tertiary alcohols as precipitating agents.* When t-butyl alcohol or isopropyl alcohol were added to the reaction mixtures, under the same reaction conditions given in (a), complexes of alkenylalkynes as in (b) were obtained.

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