Formation of $[Pt(\eta^3\text{-allyl})(TPPTS)_2]^+$ from Reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with Alkenols in Water

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Reactions of alkenols with *cis*-$Pt(Cl)_2(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) in water result in $[Pt(\eta^3\text{-allyl})(TPPTS)_2]^+$ as the exclusive platinum product with 1 equiv of oxidized alkenol. The η^3-allyl is not fluxional in water, and the syn and anti isomers can be distinguished at room temperature. For 3-buten-1-ol and 4-penten-1-ol, in addition to the η^3-allyl complex and oxidation of the alkene, catalytic isomerization of the alkene is observed. No reaction occurs for *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$, *cis*-$Pt(Cl)(THF)(P(p\text{-tolyl})_3)_2^+$, or *cis*-$Pt(THF)_2(P(p\text{-tolyl})_3)_2^{2+}$ with the alkenols in THF, indicating the importance of H_2O. Excess Cl^- inhibits the reaction. The oxidation product is selectively deuterated. These observations are combined into a proposed mechanism.

Introduction

There exist numerous reports on the synthesis of M−allyl compounds in organic solvents.[1] In 1967, Volger and Vrieze reported the first synthesis of a $Pt(\eta^3\text{-allyl})$ compound from the oxidative addition of an allylic halide with the zerovalent metal center in $CHCl_3$, as shown:[2]

$$Pt(PPh_3)_4 + R_2C{=}CH\text{-}CH_2X \rightleftharpoons [Pt(\eta^3\text{-}C_3H_4R)(PPh_3)_2]X + 2PPh_3$$

$$R = H,\ X = Cl, Br$$
$$R = CH_3,\ X = Cl$$

The authors reported that the syn and anti protons on the allyl fragment exhibited dynamic behavior in the ^1H NMR spectra when the complex was dissolved in $CDCl_3$ at room temperature.[3] Formation of a single resonance for all four protons was noted. It is well-known that the syn protons (which point away from the metal) resonate upfield from those of the anti protons (closest to the metal) in the η^3-allyl group.[1a] Therefore, they proposed that the η^3-allyl form of the compound was interconverting with the η^1-allyl form. Similar dynamic behavior is thought to occur from facile equilibration of the syn and anti protons by "dissociation of one terminus to give an η^1-allyl, followed by rotation around the new carbon−carbon single bond, and collapse to the η^3-allyl group."[1a] Many reports have focused on factors important to the interconversion, including ligand, solvent, and ion-induced conversion.[4] These data have allowed the synthesis of allyl compounds in either conformation. In a reaction analogous to the one above, Pearson and Laurent synthesized *trans*-$Pt(\eta^1\text{-allyl})(Cl)(PEt_3)_2$ by oxidative addition of the allylic halide to $Pt(PEt_3)_4$ in hexanes at room temperature.[4a] The crystal structure of a similar compound, *trans*-$Pt(\eta^1\text{-allyl})(Br)(PEt_3)_2$, was solved by Kochi et al.[5] Herein, we report the formation of stable $Pt(\eta^3\text{-allyl})$ compounds from the reaction of hydroxyl-functionalized alkenes with *cis*-$Pt(Cl)_2(TPPTS)_2$ in water.

Palladium allyls are very important in a variety of coupling reactions, including using allyl alcohols without activation.[6] A palladium allyl complex, $Pd(C_3H_5)(TPPTS)_2^+$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$), was communicated in preparation from allyl alcohol in water.[7] Use of allyl alcohol with a platinum catalyst allowed formation of *N*-allylaniline in a reaction assisted by titanium reagents.[8]

Results and Discussion

Reaction of various alkenols with *cis*-$PtCl_2(TPPTS)_2$ in H_2O results in $Pt(\eta^3\text{-allyl})(TPPTS)_2^+$.

$$PtCl_2(TPPTS)_2 + \text{alkenol} \rightarrow Pt(\eta^3\text{-allyl})(TPPTS)_2^+$$

alkenol =
allyl alcohol, 3-buten-1-ol, 4-penten-1-ol, 4-penten-2-ol, 2-buten-1-ol, 3-buten-2-ol, 1-penten-3-ol, 3-penten-2-ol

The products were characterized by NMR (^1H, ^{31}P, and ^{195}Pt) spectroscopy and comparison to PPh_3 analogues (Tables 1 and 2). In water the syn−anti fluxionality[13,14] was slowed such that

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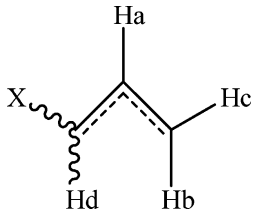
Table 1. ^{31}P and ^{195}Pt NMR Characterization of Allyl Complexes Formed

complex	$\delta(P_a)$ (ppm)	$^1J_{Pt-P}$ (Hz)	$^2J_{P-P}$ (Hz)	$\delta(P_b)$ (ppm)	$^1J_{Pt-P}$ (Hz)	$\delta(^{195}Pt)$ (ppm)
$[Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2]^+$ [a]	18.90	4014				−5391
$[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$ [1,b]	16.14	3987				
syn-$[Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2]^+$ [a]	23.03	3951	7.1	19.37	4202	−5379
syn-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]^+$ [1,b]	20.73	3939	9	17.37	4157	
anti-$[Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2]^+$ [a]	19.53	4059	9.1	18.50	3888	−5363
anti-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]^+$ [1,b]	17.54	4028	10.7	16.30	3851	
syn-$[Pt(\eta^3\text{-}C_3H_4Et)(TPPTS)_2]^+$ [a]	22.80	3970	7.1	19.14	4175	−5383
syn-$[Pt(\eta^3\text{-}C_3H_4Et)(PPh_3)_2]^+$ [1,b]	20.38	3955	9.4	17.12	4133	
anti-$[Pt(\eta^3\text{-}C_3H_4Et)(TPPTS)_2]^+$ [a]	19.60	4059	9.1	18.56	3884	−5367
anti-$[Pt(\eta^3\text{-}C_3H_4Et)(PPh_3)_2]^+$ [1,b]	17.51	4029	10.7	16.27	3845	
syn/syn-$[Pt(\eta^3\text{-}1,3\text{-}C_3H_3Me_2)(TPPTS)_2]^+$ [a]	22.06	4109				−5387
syn/syn-$[Pt(\eta^3\text{-}1,3\text{-}C_3H_3Me_2)(PPh_3)_2]^+$ [2,b,c]	20.40	4033				
$[Pt(\eta^3\text{-}1,3\text{-}C_3H_3Me_2)(TPPTS)_2]^+$ [a,d]	18.36	4002				−5402
syn/anti-$[Pt(\eta^3\text{-}1,3\text{-}C_3H_3Me_2)(TPPTS)_2]^+$ [a]	21.36	3883	5.3	18.98	4143	−5353
syn/anti-$[Pt(\eta^3\text{-}1,3\text{-}C_3H_3Me_2)(PPh_3)_2]^+$ [2,b,c]	19.00	3806		17.70	4094	

[a] Taken at room temperature in D_2O. [b] In $CDCl_3$. [c] Taken at −50 °C. [d] An additional isomer.

Table 2. ^{1}H NMR Characterization of Allyl Complexes Formed and PPh_3 Analogues



					X		
complex	Ha	Hb	Hc	Hd	H	CH_3	CH_2CH_3
$[Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2]^+$ [a,b]	5.47 (m)	3.00 (m)	3.90 (br)	3.00 (m)	3.90 (br)		
$[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]Cl$ [2,c,d]	5.91 (m)	2.94 (br)	3.79(br)	2.94 (br)	3.79 (br)		
$[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]Cl$ [2,a,c]	5.69 (m)	3.42 (m)					
$[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]BF_4$ [10,e,f]	5.42 (m)			2.95 (dd)	3.82 (d)		
syn-$[Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2]^+$ [a,b]	5.24 (dt)	2.88 (m)	3.30(br)	3.85 (m)		1.13 (br)	
syn-$Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2Cl$ [12,c,d]	5.26 (vbr)	2.80 (vbr)	3.14 (br)	3.68 (vbr)		1.26 (br-m)	
syn-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]Cl$ [12,a,c]	5.35 (dt)	3.10 (d)		3.95 (vbr)		1.27 (br-m)	
syn-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]ClO_4$ [11,e,f]	5.35 (m)	2.92 (m)	3.26 (br)	3.86 (m)		1.22 (br)	
anti-$[Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2]^+$ [a,b]	5.44 (m)	2.65 (br)	4.00 (br)	4.54 (br)		0.90 (br)	
anti-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]Cl$ [12,c,d]		2.50 (vbr)	4.02 (br)	4.34 (vbr)		1.08 (br-m)	
anti-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]Cl$ [12,a,c]	5.58 (m)			4.40 (vbr)		1.05 (br-m)	
anti-$[Pt(\eta^3\text{-}C_3H_4Me)(PPh_3)_2]ClO_4$ [11,e,f]	5.52 (m)	2.63 (dd)	3.94 (br)	4.44 (vbr)		1.01 (br)	
syn-$[Pt(\eta^3\text{-}C_3H_4Et)(TPPTS)_2]^+$ [a,b]	5.22 (dt)	2.88 (m)	3.43 (br)	3.81 (m)			1.21 (br), 0.67 (t)
syn-$[Pt(\eta^3\text{-}C_3H_4Et)(PPh_3)_2]BF_4$ [9,c]	5.28 (m)	2.92 (m)	3.29 (br)	3.75 (m)			1.16 (br), 0.76 (t)
anti-$[Pt(\eta^3\text{-}C_3H_4Et)(TPPTS)_2]^+$ [a,b]	5.43 (m)	2.65 (br)	4.05 (br)	4.47 (br)			1.13 (br), 0.50 (t)
anti-$[Pt(\eta^3\text{-}C_3H_4Et)(PPh_3)_2]BF_4$ [9,c]	5.58 (m)	2.49 (m)	4.00 (br)	4.30 (br)			1.36 (br), 0.64 (t)

[a] Taken at room temperature. [b] Taken in D_2O. [c] Taken in $CDCl_3$. [d] Taken at −50 °C. [e] Taken in CD_2Cl_2. [f] Taken at 30 °C.

the resonances could be distinguished at room temperature. Table 3 shows the specific platinum allyl products for each alkenol. Because of significant overlap, TOCSY was used for ^{1}H NMR assignments (Figure 1 and Supporting Information).

Platinum(II) complexes not containing a hydride do not react with allyl alcohol or allyl halides to give Pt(II) allyl compounds in nonaqueous solvents. We verified this lack of reactivity by examining *cis*-$PtCl_2(P(p\text{-tolyl})_3)_2$, *cis*-$PtCl(P(p\text{-tolyl})_3)_2(THF)^+$, and *cis*-$Pt(P(p\text{-tolyl})_3)_2(THF)_2^{2+}$ with allyl alcohol in dry THF. No reaction was observed for any of these complexes in dry THF. Thus, water plays a key role.

Table 3. Platinum Allyl Products for Various Alkenols[a]

alkenol	product(s)
C_3H_5OH	$Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2^+$
3-buten-1-ol	*syn*- and *anti*-$Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2^+$ (2.3:1)
4-penten-1-ol	*syn*- and *anti*-$Pt(\eta^3\text{-}C_3H_4Et)(TPPTS)_2^+$ (2.3:1)
4-penten-2-ol	*syn/syn*- and *syn/anti*-$Pt(\eta^3\text{-}C_3H_3Me_2)(TPPTS)_2^+$ + additional isomer (1:3:1)
2-buten-1-ol	*syn*- and *anti*-$Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2^+$ (2.3:1)
3-buten-2-ol	*syn*- and *anti*-$Pt(\eta^3\text{-}C_3H_4Me)(TPPTS)_2^+$ (2.3:1)
1-penten-3-ol	*syn*- and *anti*-$Pt(\eta^3\text{-}C_3H_4Et)(TPPTS)_2^+$ (2.3:1)
3-penten-2-ol	*syn/anti*- and *syn/syn*-$Pt(\eta^3\text{-}C_3H_3Me_2)(TPPTS)_2$ (3:1)

[a] Relative amounts are given as ratios.

Formation of $Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2^+$ from allyl alcohol in water is accompanied by stoichiometric formation of 1-hydroxyacetone:

$$PtCl_2L_2 + 2CH_2{=}CHCH_2OH + H_2O \rightarrow Pt(\eta^3\text{-allyl})L_2^+ + CH_3C(O)CH_2OH + H^+ + 2Cl^-$$

$$L = TPPTS$$

Clean formation of 1-hydroxyacetone is in contrast to Wacker

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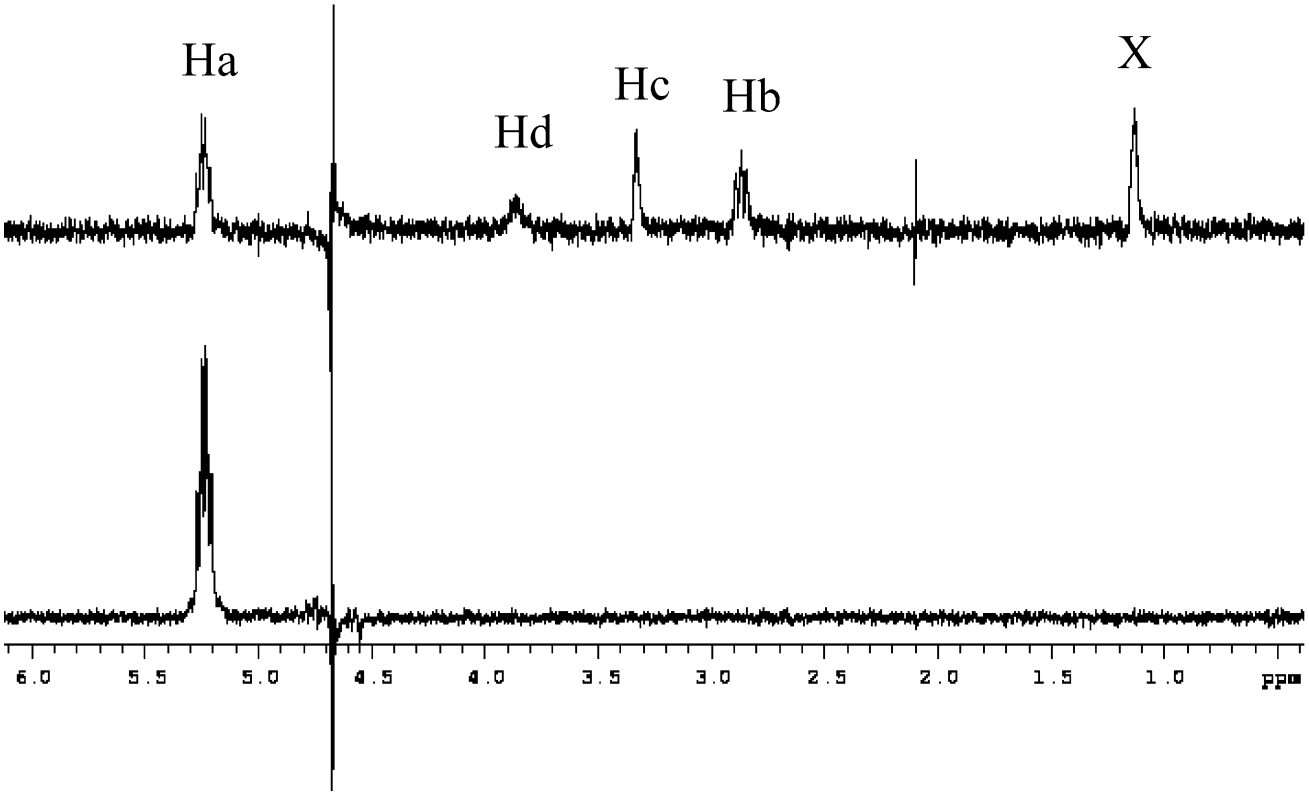


Figure 1. ^{1}H TOCSY NMR spectrum of the isolated product from the reaction of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ with 3-buten-1-ol. The bottom spectrum shows the particular resonance being pulsed (in this case δ 5.24 ppm). The top spectrum is the effect of pulsing that particular resonance. The resonances that appear represent the protons on the allylic fragment of *syn*-Pt(η^3-C$_4$H$_7$)(TPPTS)$_2^+$. The labeling scheme is taken from Table 2 (signal at ~2 ppm is noise).

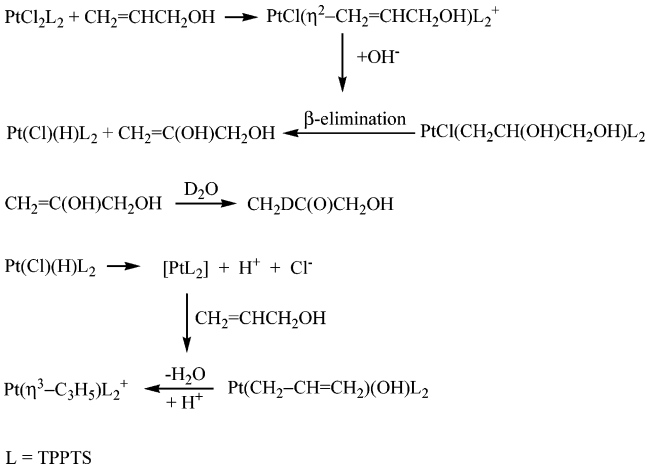
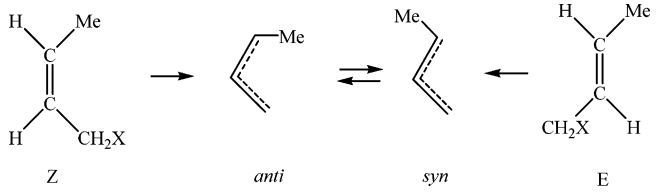


Figure 2. Scheme for the reaction of allyl alcohol with *cis*-PtCl$_2$(TPPTS)$_2$.

oxidation of allyl alcohol, which forms HOCH$_2$CH$_2$CHO, among other products.[15] When the reaction of *cis*-PtCl$_2$(TPPTS)$_2$ with allyl alcohol was examined in D$_2$O, CH$_2$DC(O)CH$_2$OH was formed; this again is in contrast with Wacker oxidations, where deuterium is usually not incorporated from D$_2$O.[16] Added chloride significantly slows the reaction of allyl alcohol with *cis*-PtCl$_2$(TPPTS)$_2$ in water.

These observations are most consistent with the scheme shown in Figure 2. Coordination through the double bond and attack on the cationic complex by OH$^-$ are consistent with previous studies[17] and with the Wacker process.[15,16] Perhaps because of steric congestion or electronic differences, the alkene complex resulting from β-hydride elimination in our case is not stable and the enol is released into solution, rearranging to the observed keto species 1-hydroxyacetone. The formed platinum hydride has been shown to be unstable in water and can be considered a precursor of Pt(0) in aqueous solution.[18] Pt(TPPTS)$_2$ can oxidatively add allyl alcohol. Dissociation of OH$^-$ (or protonolysis and dissociation of H$_2$O) and $\eta^1-\eta^3$ rearrangement of the allyl give the observed products. The reactions in Figure 2 generate 1 equiv of H$^+$, consistent with the observed pH change from 3 to 2.

Scheme 1



We recently published a series of reactions of *cis*-PtCl$_2$(TPPTS)$_2$ with ethylene, propene, butenes, and 1-hexene in water.[17a] Oxidation products (acetaldehyde, acetone, etc.) were produced in stoichiometric amounts with *trans*-Pt(Cl(H)(TPPTS)$_2$, similar to the initial reaction described in Figure 2. For the alkenols 3-buten-1-ol, 4-penten-1-ol, and 3-buten-2-ol, stoichiometric quantities of the expected oxidation products are

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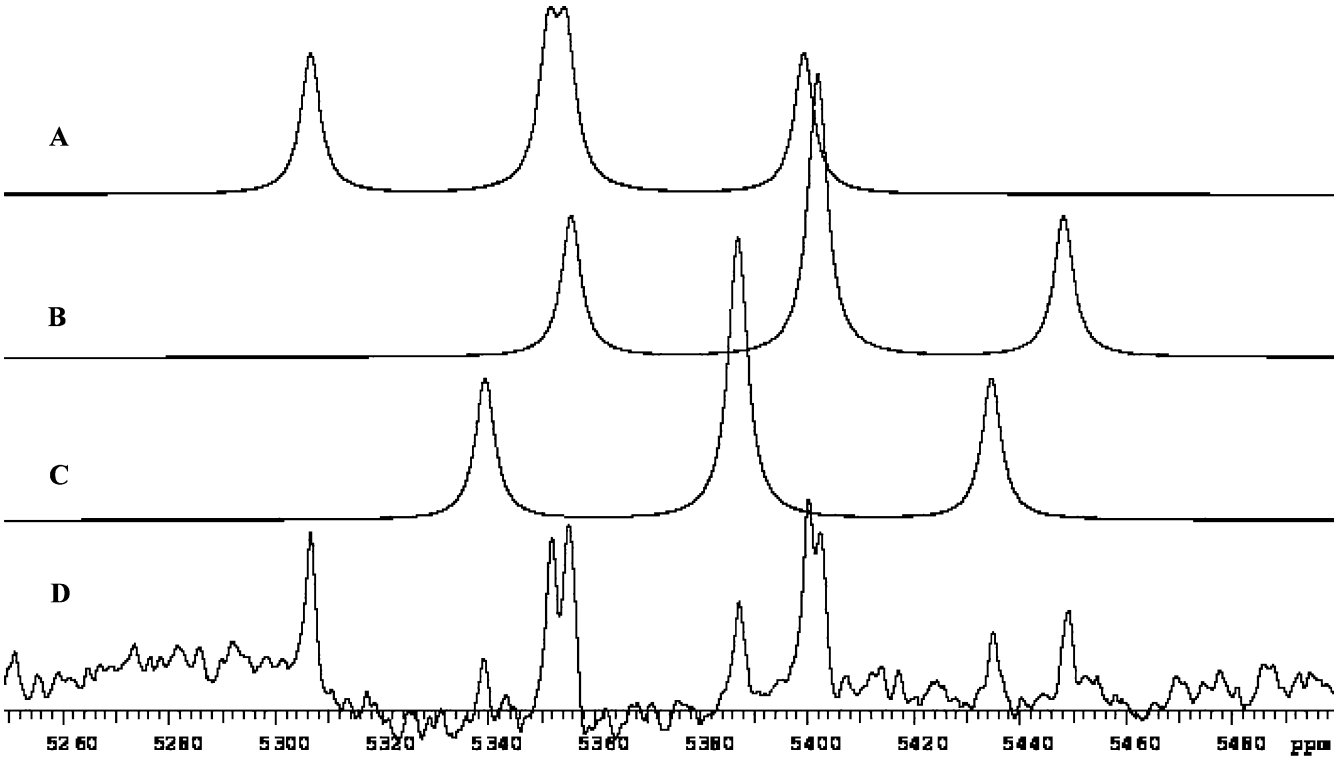

Figure 3. ^{195}Pt NMR spectrum (D) of the solution from the reaction of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ with 4-penten-2-ol. The top three spectra (A−C) were simulated to explain the appearance of the signals in the actual spectrum on the bottom. The chemical shifts and coupling constants were taken from the data in Table 1 for the species of type *syn*/*syn*-Pt(η^3-C$_5$H$_9$)(TPPTS)$_2^+$ (C), additional isomer of Pt(η^3-C$_5$H$_9$)(TPPTS)$_2^+$ (B), *syn*/*anti*-Pt(η^3-C$_5$H$_9$)(TPPTS)$_2^+$.

also observed: 4-hydroxy-butan-2-one, 5-hydroxy-pentan-2-one, and 3-hydroxy-butan-2-one, respectively. Thus, the mechanism outlined in Figure 2 is indicated for these alkenols also.

Reactions of 3-buten-1-ol and 4-penten-1-ol with *cis*-PtCl$_2$(TPPTS)$_2$ are accompanied by catalytic isomerization to 2-buten-1-ol and 3-penten-1-ol, respectively. Such isomerization would be expected from a platinum hydride intermediate or could occur through an allyl mechanism.[19]

Other alkenols such as 2-buten-1-ol, 4-penten-2-ol, 1-penten-3-ol, and 3-penten-2-ol give allyl products, as indicated in Table 3. These cases required large excesses of the alkenol, and overlap precluded identification of organic products.

The stereochemistry of allyl formation has been studied for many years on many different transition-metal complexes.[2−5,14,20] While the formation of allyl complexes from Pt(II) and allyl alcohol is unusual, the stereochemistries are typical. Table 3 and Scheme 1 provide a summary of the main stereochemical results. In the absence of isomerization, the (*E*)- and (*Z*)-alkenes are reported to give allyls, syn and anti, respectively, in greater than 95% purity.[14c] The anti−syn isomerization is strongly solvent dependent, with the slowest isomerization in water.[14c] Usually the syn allyl is thermodynamically favored.[14,20] Our results fit this, since the syn:anti ratio is (2−3):1 for all of the allyls.

Only in the 1,3-dimethylallyl formed from 4-penten-2-ol is there a stereochemical anomaly. Literature reports from several preparations show that 1,3-dimethylallyl is formed as the syn/syn:syn/anti species in a 1:3 ratio;[14c,20d,f−h,j,k] we see this ratio for 3-penten-2-ol. However, for 4-penten-2-ol we see an additional product that has a singlet ^{31}P and a triplet ^{195}Pt. The coupling constants and the ^{195}Pt chemical shift of −5402 ppm are as expected for an allyl bis-phosphine complex.[21] The ^{195}Pt NMR signals are shown and simulated in Figure 3.

Formation of allyl complexes from Pd(0) or Pt(0) is well precedented, but formation of η^3-allyl complexes from Pd(II) or Pt(II) complexes is not as well understood.[12,20l] Ozawa et al.[20l] recently reported reactions of Pd(H)(OTf)LL and Pt(H)(OTf)LL (LL = bidentate phosphine ligand) with allylic alcohols to form (η^3-allyl)ML$^+$ complexes that provide a nice precedent for our suggestion at the bottom of Figure 2. For M = Pt the reaction gave good yields of the η^3-allyl complexes after 3 h at 50 °C.[20l] Such reactions, starting from the hydride, provide a route to η^3-allyl complexes without formation of another product.

Reactions of PtCl$_4^{2-}$ with allyl alcohol and even allyl sulfonate were reported to provide the olefin complex, PtCl$_3$(olefin)$^-$, not the allyl complex.[22] Reaction of PdCl$^+$, formed from PdCl$_2$(CH$_3$CN)$_2$ and 1 equiv of AgOTf, with allylic

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alcohols gave η^3-allyl complexes with no aldehyde products but with formation of tetrahydrofuran derivatives that produced a Pd hydride complex.[23] Two studies of $PdCl_4^{2-}$ also suggest formation of a Pd hydride prior to η^3-allyl formation.[15a,24] Our reaction is consistent with these prior studies, except that in water with $PtCl_2(TPPTS)_2$, the alkene can be nucleophilically attacked and generate the $Pt(Cl)(H)(TPPTS)_2$ through a β-hydride elimination (Figure 2). The clean formation of monodeuterated oxidation product provides good evidence for β-hydride elimination and dissociation of the enol from platinum with the deuterium added in the enol → keto rearrangement. No deuterium is incorporated into the isomerization products.

Conclusion

We have detailed the formation of $[Pt(\eta^3\text{-allyl})(TPPTS)_2]^+$ species from the reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with various hydroxyl-functionalized alkenes. The characterizations of these species agree very well with those of their PPh_3 analogues. A mechanism was proposed which explains the observations made throughout, such as formation of a Pt−H species, characterization of alkene oxidation products, effect of added chloride, etc. Since allylic compounds are important in a variety of reactions, i.e., allylic alkylation, such traditional organic reactions may take place in water as a result,[1b] providing an example of benign synthesis.

Experimental Section

Materials. All substrates (allyl alcohol, 3-buten-1-ol, 2-buten-1-ol (mixture of isomers), 3-buten-2-ol, 4-penten-1-ol, 1-penten-3-ol, 4-penten-2-ol, and 3-penten-2-ol (predominately trans)) were purchased from Aldrich Chemical Co. and were used as received. D_2O and d_8-THF were purchased from Cambridge Laboratory Isotopes and used as received. *cis*-$Pt(Cl)_2(TPPTS)_2$[17b] and *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$[25] were synthesized according to literature procedures.

Solvents. Water was triply distilled and degassed with N_2 prior to use. Diethyl ether and THF were purchased from VWR; the THF was dried by refluxing over Na/benzophenone overnight, followed by distilling under N_2. Absolute EtOH was purchased from Pharmco and used as received.

pH Buffers. The pH 4 buffer was composed of a 0.05 M solution of sodium biphthalate. The pH 7 buffer was composed of a solution of 0.021 M NaH_2PO_4 and 0.029 M Na_2HPO_4. The pH 10 buffer was composed of a solution of 0.025 M $NaHCO_3$ and 0.025 M Na_2CO_3. All three buffers were purchased from VWR and diluted to the appropriate volume using triply distilled water.

Methods. ^1H , ^{31}P, and ^{195}Pt NMR spectra were recorded on a Varian XL 400 NMR spectrometer. 1D ^1H TOCSY and 2D ^1H COSY NMR were recorded on a 500 MHz Varian NMR spectrometer. ^{31}P NMR spectra (161.89 Hz) were proton decoupled and referenced to an external standard of 85% phosphoric acid in D_2O. ^{195}Pt NMR (85.75 MHz) spectra were referenced to an external standard of 0.2 M K_2PtCl_4 (in 0.4 M KCl/D_2O), which was set at −1627 ppm.[26] A coaxial inner cell filled with d_6-DMSO was used to take NMR spectra in H_2O.

A mass spectrum of $[Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2]Cl$ was recorded by the Mass Spectrometry and Proteomics Facility of Ohio State University using Q-TOF 2 nanospray.

pH measurements were performed using a Fischer Scientific Accumet basic pH meter by Denver Instruments Inc. with a semimicro glass pH electrode with a silver/silver chloride reference electrode. The pH electrode was calibrated at pH 4, 7, and 10 using pH buffers.

Synthesis of $[Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2]Cl$. Into a 25 mL Schlenk flask was placed 0.1217 g (0.458 mmol) of $PtCl_2$, 0.5709 g (0.917 mmol) of TPPTS, and a small stir bar. The flask was evacuated and back-filled with N_2 three times, after which 10 mL of triply distilled water was added to the flask via airtight syringe. The flask was immersed in a preheated oil bath at 70 °C. After about 1.5 h, the solid $PtCl_2$ had completely dissolved and 500 μL of allyl alcohol (7.35 mmol) was added to the flask. The resulting solution was stirred at 70 °C for 15 h. After the allotted time, the contents of the flask were added to a 250 mL round-bottom flask containing ∼100 mL of EtOH. A white solid immediately precipitated. The solvent was removed in vacuo, and the white solid was collected and placed into a glass vial. Yield: 0.521 g (75% based on moles of $PtCl_2$). The mass spectrum shows the molecular ion for the cation centered around 1373 amu with the usual platinum distribution.

^{195}Pt NMR (D_2O, room temperature): δ −5391 (t, $^1J_{Pt-P} = 4014$ Hz). $^{31}P\{^1H\}$ NMR (D_2O, room temperature): δ 18.90 (s, $^1J_{Pt-P} = 4014$ Hz). ^1H NMR (D_2O, room temperature): δ 7.8−7.0 (m, $[Pt(\eta^3\text{-}C_3H_5)(TPPTS)_2]Cl$, 24H), 5.47 (m, meso H, 1H), 3.90 (br, syn H's, 2H), 3.00 (m, anti H's, 2H).

Reaction Performed in Carius Tubes. These reactions were conducted in 10 mL Carius tubes, modified with a 14/20 glass joint.

(a) Reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with Excess Allyl Alcohol. Into a 10 mL modified Carius tube was placed 0.1264 g (0.0836 mmol) of *cis*-$Pt(Cl)_2(TPPTS)_2$, a small stir bar, and 1.0 mL of triply distilled water. Upon complete dissolution of the solid, 20 drops of an alkenol was added to the solution. The tube was then attached to the high-vacuum line and subjected to three freeze−pump−thaw cycles, after which the tube was flame-sealed under vacuum. The sealed tube was placed into a constant-temperature bath at 82 °C and stirred at this temperature for 3 h. After the allotted time, a 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{195}Pt and ^{31}P NMR spectroscopy. Results are given in Tables 1 and 2.

To isolate the allyl product, the contents of the tube were transferred to a 100 mL round-bottom flask containing ∼50 mL of EtOH. An off-white precipitate was immediately formed. The flask was attached to the rotary evaporator and the solvent removed in vacuo. The residue was redissolved in 1.0 mL of triply distilled water and precipitated again as described. After removal of the solvent, the off-white residue was dissolved in 0.5 mL of D_2O and analyzed by ^{31}P and ^1H NMR spectroscopy. Results are given in Tables 1 and 2. Discussion of the NMR results is given in the Supporting Information.

(b) Reaction of *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$ with 3-Buten-1-ol at Room Temperature. In the drybox, 0.0560 g (0.0640 mmol) of *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$ was placed into a 15 mL Schlenk flask, along with a small stir bar. To the flask was then added 4.0 mL of dry THF. Upon stirring, a suspension was produced. To the suspension was added 3 drops of 3-buten-1-ol from a glass pipet. The flask was sealed with a rubber septum and stirred at room temperature for 21.5 h. After the allotted time, a 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{31}P and ^1H NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (THF, d_8-THF insert, room temperature): δ 27.0 (s, O*P*$(p\text{-tolyl})_3$, 1.5%), 19.9 (s, *trans*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$, 16%), 14.2 (s, *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$, 82.5%).

(c) Reaction of *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$ with 3-Buten-1-ol at 60 °C. In the drybox, 0.0580 g (0.0663 mmol) of *cis*-$Pt(Cl)_2(P(p\text{-tolyl})_3)_2$, a small stir bar, and 4.0 mL of dry THF were placed into a 10 mL modified Carius tube. To the mixture was added 3 drops of 3-buten-1-ol from a glass pipet. The tube was fitted with an

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adapter to the high-vacuum line, sealed, and removed from the drybox. The tube was then attached to the high-vacuum line and subjected to three freeze−pump−thaw cycles, after which the tube was flame-sealed under vacuum. The sealed tube was placed into a constant-temperature bath at 60 °C and stirred at this temperature for 3.5 h. After the allotted time, a 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{31}P and ^{1}H NMR spectroscopy.

^{31}P{^{1}H} NMR (THF, d_8-THF insert, room temperature): δ 27.0 (s, O*P*(*p*-tolyl)$_3$, 2.5%), 19.9 (s, *trans*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 15.5%), 14.2 (s, *cis*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 82%).

(d) Reaction of *cis*-Pt(Cl)$_2$(P(*p*-tolyl)$_3$)$_2$, 1 Equiv of AgNO$_3$, and 3-Buten-1-ol. Into a 25 mL Schlenk flask, wrapped in aluminum foil, was placed 0.0964 g (0.110 mmol) of *cis*-Pt(Cl)$_2$-(P(*p*-tolyl)$_3$)$_2$, a stir bar, and 15 mL of dry THF. To the flask was then added 0.0186 g (0.110 mmol) of AgNO$_3$. An off-white solid immediately precipitated. The resulting mixture was stirred at room temperature for 1 h. After the allotted time, the solid (AgCl) was removed by gravity filtration and the filtrate collected in a 150 mL round-bottom flask. A 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{31}P NMR spectroscopy.

^{31}P{^{1}H} NMR (THF, d_8-THF insert, room temperature): δ 32.1 (s, unidentified, 3%), 20.0 (s, *trans*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 9%), 16.6 (d, $^{1}J_{Pt-P}$ = 3858 Hz, *cis*-[Pt(THF)(Cl)(*P*(*p*-tolyl)$_3$)$_2$]$^{+}$), 1.6 (d, $^{1}J_{Pt-P}$ = 3896 Hz, *cis*-[Pt(THF)(Cl)(*P*(*p*-tolyl)$_3$)$_2$]$^{+}$, 81%), 15.9 (s, unidentified, 1%), 12.0 (s, unidentified, 2%), 2.9 (s, unidentified, 3%).

The remaining solution was placed under vacuum and the solvent removed to produce a brown solid. To the solid was added 1.5 mL of dry THF to redissolve it. The resulting brown solution was placed into a 10 mL modified Carius tube, equipped with a small stir bar. To the solution was added 3 drops of 3-buten-1-ol from a glass pipet. The tube was then attached to the high-vacuum line and subjected to three freeze−pump−thaw cycles, after which the tube was flame-sealed under vacuum. The sealed tube was placed into a constant-temperature bath at 60 °C and stirred at this temperature for 3 h. After the allotted time, a 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{31}P and ^{1}H NMR spectroscopy.

^{31}P{^{1}H} NMR (THF, d_8-THF insert, room temperature): δ 28.2 (s, O*P*(*p*-tolyl)$_3$, 34%), 19.8 (s, *trans*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 1%), 16.6 (d, $^{1}J_{Pt-P}$ = 3858 Hz, *cis*-[Pt(THF)(Cl)(*P*(*p*-tolyl)$_3$)$_2$]$^{+}$), 1.6 (d, $^{1}J_{Pt-P}$ = 3896 Hz, cis-[Pt(THF)(Cl)(*P*(*p*-tolyl)$_3$)$_2$]$^{+}$, 53%), 13.9 (s, *cis*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 12%).

(e) Reaction of *cis*-Pt(Cl)$_2$(P(*p*-tolyl)$_3$)$_2$, 2 Equiv of AgNO$_3$, and 3-Buten-1-ol. Into a 25 mL Schlenk flask, wrapped in aluminum foil, was placed 0.1112 g (0.127 mmol) of *cis*-Pt(Cl)$_2$-(P(*p*-tolyl)$_3$)$_2$, a stir bar, and 20 mL of dry THF. To the flask was then added 0.0446 g (0.262 mmol) of AgNO$_3$. An off-white solid immediately precipitated. The resulting mixture was allowed to stir at room temperature for 1 h. After the allotted time, the solid (AgCl) was removed by gravity filtration and the filtrate collected in a 150 mL round-bottom flask. A 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{31}P NMR spectroscopy.

^{31}P{^{1}H} NMR (THF, d_8-THF insert, room temperature): δ 20.8 (s, *trans*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 4%), 3.4 (s, $^{1}J_{Pt-P}$ = 4003 Hz, *cis*-[Pt(THF)$_2$(*P*(*p*-tolyl)$_3$)$_2$]$^{2+}$, 96%).

The remaining solution was placed under vacuum and the solvent removed to produce a brown solid. To the solid was added 2.5 mL of dry THF to redissolve it. The resulting brown solution was placed into a 10 mL modified Carius tube, equipped with a small stir bar. To the solution was added 3 drops of 3-buten-1-ol from a glass pipet. The tube was then attached to the high-vacuum line and subjected to three freeze−pump−thaw cycles, after which the tube was flame-sealed under vacuum. The sealed tube was placed into a constant-temperature bath at 60 °C and stirred at this temperature for 3 h. After the allotted time, a 0.5 mL aliquot of the resulting solution was placed into an NMR tube and analyzed by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy.

^{31}P{^{1}H} NMR (THF, d_8-THF insert, room temperature): δ 20.3 (s, *trans*-Pt(Cl)$_2$(*P*(*p*-tolyl)$_3$)$_2$, 1%), 17.1 (d, *cis*-[Pt(THF)(Cl)(*P*(*p*-tolyl)$_3$)$_2$]$^{+}$), 2.1 (d, *cis*-[Pt(THF)(Cl)(*P*(*p*-tolyl)$_3$)$_2$]$^{+}$, 12%), 15.9 (s, unidentified, 7%), 14.0 (s, unidentified, 4%), 3.4 (s, $^{1}J_{Pt-P}$ = 4003 Hz, *cis*-[Pt(THF)$_2$(*P*(*p*-tolyl)$_3$)$_2$]$^{2+}$, 76%).

General Procedure for Deuterium-Labeling Studies. In each reaction, ∼ 22 mg of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ was placed into the glass vessel, equipped with a small stir bar, along with either 1 mL of H_2O or D_2O. For allyl alcohol, 10 equiv of the substrate was added, while in the 3-buten-1-ol and 4-penten-1-ol reactions, 20 equiv of the substrate was utilized. The substrates were added under N_2 purge to the catalyst solution. Each reaction was sealed under a static pressure of N_2 using a rubber septum. Reaction mixtures for allyl alcohol and 3-buten-1-ol were heated to 80 °C for 3 h. Those for 4-penten-1-ol were left at room temperature for 22 h. After the allotted time, a 0.5 mL aliquot of the resulting solution was removed via pipet under N_2 purge and placed into an NMR tube. Once the solution was cooled to room temperature, both ^{31}P and ^{1}H spectra were recorded using a d_6-DMSO filled coaxial inner cell for those solutions done in H_2O.

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Supporting Information Available: Text and figures giving a detailed NMR discussion, the effect of chloride and water, and deuterium incorporation experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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