4830 *Organometallics* **2007,** *26,* 4830−4834

Water-Soluble Ethylene Complex with Platinum: Water Stability and Reaction with Diethylamine

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Received May 9, 2007

A water-soluble ethylene complex of platinum, *cis*-$PtCl_2(TPPTS)(C_2H_4)$, is prepared and characterized by spectroscopic methods in comparison to the PPh_3 analogue. The ethylene complex is stable in water from pH 0 to 9. At pH 10.5 the complex decomposes to C_2H_5OH and CH_3CHO over a few days. Reaction of *cis*-$PtCl_2(TPPTS)(C_2H_4)$ with $NHEt_2$ in DMF gives *cis*-$PtCl_2(TPPTS)(CH_2CH_2NHEt_2)$, which was characterized by NMR. Thus the water-soluble ethylene complex, which is stable in water to pH 9, is susceptible to nucleophilic attack.

A number of articles and reviews point to the potential environmental benefits of water as a solvent to replace organic solvents in organometallic and catalytic reactions.[1,2] In addition to environmental benefits, several studies have shown that water as a solvent accelerates reactions, providing a kinetic benefit to water as a solvent.[1−3]

From Zeiss's time,[4] platinum complexes have had a special role in understanding ethylene as a ligand. With the industrial use of the Wacker process, catalyzed by palladium salts in water, many studies focused on platinum and palladium reactions with C_2H_4 in water.[5] The following reactions illustrate different products from similar platinum complexes reacting in water with ethylene.[6] These reactions show a range of organic products from similar reactants and indicate the diverse reactions that may be expected for alkenes in aqueous solution.

$$PtCl_3(C_2H_4)^- \xrightarrow{H_2O} CH_3CHO + 2HCl + Cl^- \qquad (1)$$

$$2PtCl_4^{2-} + 4C_2H_4 \xrightarrow{H_2O} Pt_2(C_2H_4)_2(C_2H_5)_2(\mu\text{-}Cl)_2 + 2HO^- + 2Cl^- \qquad (2)$$

$$PtCl_3(C_2H_4)^- \xrightarrow{H_2O} PtCl_3(C_2H_4OH)^{2-} \xrightarrow{\text{oxidation}} HOCH_2CH_2OH \qquad (3)$$

Pt(0) complexes with alkenes are readily prepared and are reasonably stable.[7] Pt(II) complexes, other than the commonly used starting complexes $Pt(cod)X_2$, are less stable, frequently undergoing additional reactions.[8] Five-coordinate alkene complexes of Pt(II) have been studied.[9] The one class of square-planar Pt(II) alkene complexes, other than Zeiss's salt, that have reasonable stability and have been examined are $PtCl_2L(\eta^2$-alkene),[10−14] where L = phosphine or N-donor. Primarily, these were structural studies with the only reported reactions being alkene displacement[10,14] and diethylamine attack.[10,11] Only for aminoacid complexes[13] were the complexes examined in water.

In this article we prepare and spectroscopically characterize a water-soluble Pt(II) alkene complex, $PtCl_2(TPPTS)(C_2H_4)$, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$. This complex is stable in H_2O from pH 0 to 9; reactions at pH 10.5 and with $NHEt_2$ are described.

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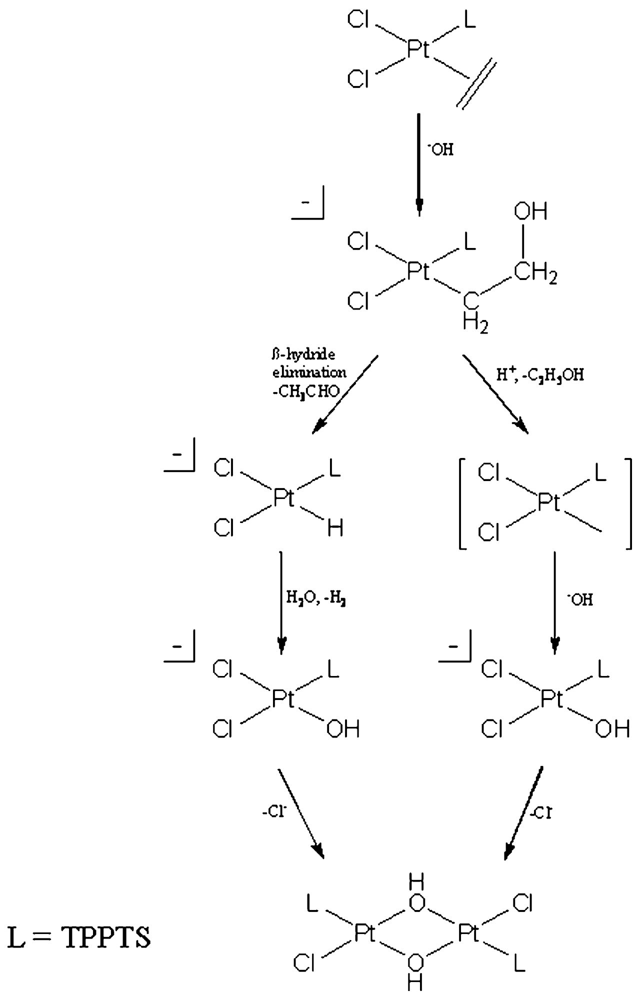
Scheme 1



Experimental Section

Materials. The following chemicals were used in the syntheses: K_2PtCl_4 and $H_2PtCl_6{\cdot}H_2O$ were purchased from Strem Chemicals; PPh_3 was purchased from Aldrich Chemical Co. and recrystallized from ethanol. $PtCl_2$[15] and TPPTS[16,17] were synthesized by literature procedures. Deuterated solvents, dimethylformamide (C_3D_7ON), and methanol (CD_3OD) were purchased from Aldrich Chemical Co. Triply distilled H_2O was available from Dr. G. Nancollas's lab. Ar and N_2 were purchased from Praxair. Ethylene, research purity (99.999%), was purchased from Matheson. All solvents were purchased from Aldrich Chemical Co. and used as received without further purification.

Instrumentation. ^{1}H, ^{31}P, and ^{195}Pt spectra were recorded using a Varian VXR 400 MHz NMR spectrometer. ^{31}P NMR spectra were ^{1}H decoupled and referenced to an external sample of 85% H_3PO_4 in D_2O (reference was set to 0.00 ppm). ^{195}Pt NMR spectra were referenced to an external sample of 0.2 M K_2PtCl_4 (in 0.4 KCl/D_2O), in which the reference was set to −1627.00 ppm.[18] All ^{1}H spectra were referenced to TMS (reference set to 0.00 ppm). Aromatic protons in the region of 7−8 ppm were excluded from discussion for simplicity. All chemical shifts are reported in parts per million (ppm), and all coupling constants (J) are in Hz. Whenever possible ^{1}H and ^{31}P spectra were integrated and relative abundance for each species present in a given sample was assigned.

Table 1. NMR Characterization of *cis*-$PtCl_2L(C_2H_4)$

	L = TPPTS[a]	L = PPh_3[10] [b]
^{31}P	14.7 ppm (J_{P-Pt} = 3294 Hz)	14.6 ppm (J_{P-Pt} = 3295 Hz)
^{1}H[c]	4.1 (br)	4.1 (br)
^{195}Pt	4048 ppm (J_{P-Pt} = 3294 Hz)	4048 (J_{P-Pt} = 3295 Hz)

[a] ^{1}H NMR spectrum was taken in CD_3OD. [b] ^{1}H NMR spectrum was taken in $CDCl_3$. [c] Aromatic resonances were also observed.

***cis*-$PtCl_2(TPPTS)(C_2H_4)$.** Equimolar amounts of $PtCl_2$ (0.96 mmol, 0.29 g) and TPPTS (0.96 mmol, 0.55 g) were dissolved in 20 mL of DMF. The reactants were placed into a 50 mL lipless beaker, which was pressurized in a Parr apparatus with 500 psi of ethylene. The reaction mixture was stirred under ethylene pressure for 5 days. Afterward the bomb was depressurized and the solution was filtered on a fine grade frit. The solution was transferred from a filter flask to a 500 mL beaker. Precipitation of the product was induced with 300 mL of diethyl ether. The obtained product was collected on a medium grade frit and exhibited a paste-like consistency and was further washed with copious amounts of pentane. The white solid was dried *in vacuo* overnight and stored under Ar. Overall yield of 48% was achieved.

$^{31}P\{^{1}H\}$ NMR (D_2O; δ (ppm)): 14.72 (s, $^{1}J_{P-Pt}$ = 3294). ^{1}H NMR (D_2O; δ (ppm)): 4.05 (br, 4H). ^{195}Pt NMR (D_2O; δ (ppm)): 4047.5 (d, $^{1}J_{P-Pt}$ = 3294).

***cis*-$PtCl_2(TPPTS)(C_2H_4NHEt_2)$.** A 20 mL Schlenk flask was loaded with 0.104 g (0.11 mmol) of *cis*-$PtCl_2(TPPTS)(C_2H_4)$ and 4 mL of DMF, capped with a rubber septum, and backfilled with N_2. The flask was placed in an acetone bath cooled with dry ice, and the temperature of −35 ± 5 °C was maintained throughout the reaction. A 2-fold excess of diethylamine in dichloromethane was added via syringe into a light brown solution of platinum complex. The reaction was stirred for 45 min, at which point 10 mL of acetone was added and the brown solution turned milky gray. The reaction mixture was allowed to reach room temperature, and the solution was filtered through a fine sintered frit. The gray solid was washed with 5 × 30 mL portions of ice-cold acetone and left to dry *in vacuo* overnight.

$^{31}P\{^{1}H\}$ NMR (CD_3OD; δ (ppm)): 14.11 (s, $^{1}J_{(P-Pt)}$ = 4383). ^{1}H NMR (CD_3OD; δ (ppm)): 0.51 (m, $J_{(H-Pt)}$ = 82.79, $J_{(H-P)}$ = 2.79, and $J_{(H-H)}$ = 7.39, 2H PtCH_2), 4.31 (t, $J_{(H-H)}$ = 7.59, 2H, $PtCH_2$$CH_2$), 2.94 (m, 4H), 1.59 (m, 6H).

Results and Discussion

The water-soluble C_2H_4 complex *cis*-$PtCl_2(TPPTS)(C_2H_4)$ could be prepared by two procedures, direct reaction of equimolar quantities of $PtCl_2$ and TPPTS in DMF followed by pressurization with C_2H_4,

$$\mathrm{PtCl_2 + TPPTS \xrightarrow[\text{DMF}]{C_2H_4\ (500\ psi)} \mathit{cis}\text{-}PtCl_2(TPPTS)(C_2H_4)} \qquad (4)$$

or by C_2H_4 displacement of DMSO from $PtCl_2(TPPTS)(DMSO)$ under pressure. The former gave a better yield and is the preferred synthesis. In reaction 4 any solvent other than DMF gave a mixture of products.

As with many TPPTS complexes, *cis*-$PtCl_2(TPPTS)(C_2H_4)$ does not readily crystallize. This complex was characterized spectroscopically, based on comparison to the structurally characterized analogue *cis*-$PtCl_2(PPh_3)(C_2H_4)$.[10,11] Table 1 provides the ^{1}H, ^{31}P, and ^{195}Pt NMR comparisons of *cis*-$PtCl_2(TPPTS)(C_2H_4)$ and *cis*-$PtCl_2(PPh_3)(C_2H_4)$. The characterization data provide strong support for the complex. Especially

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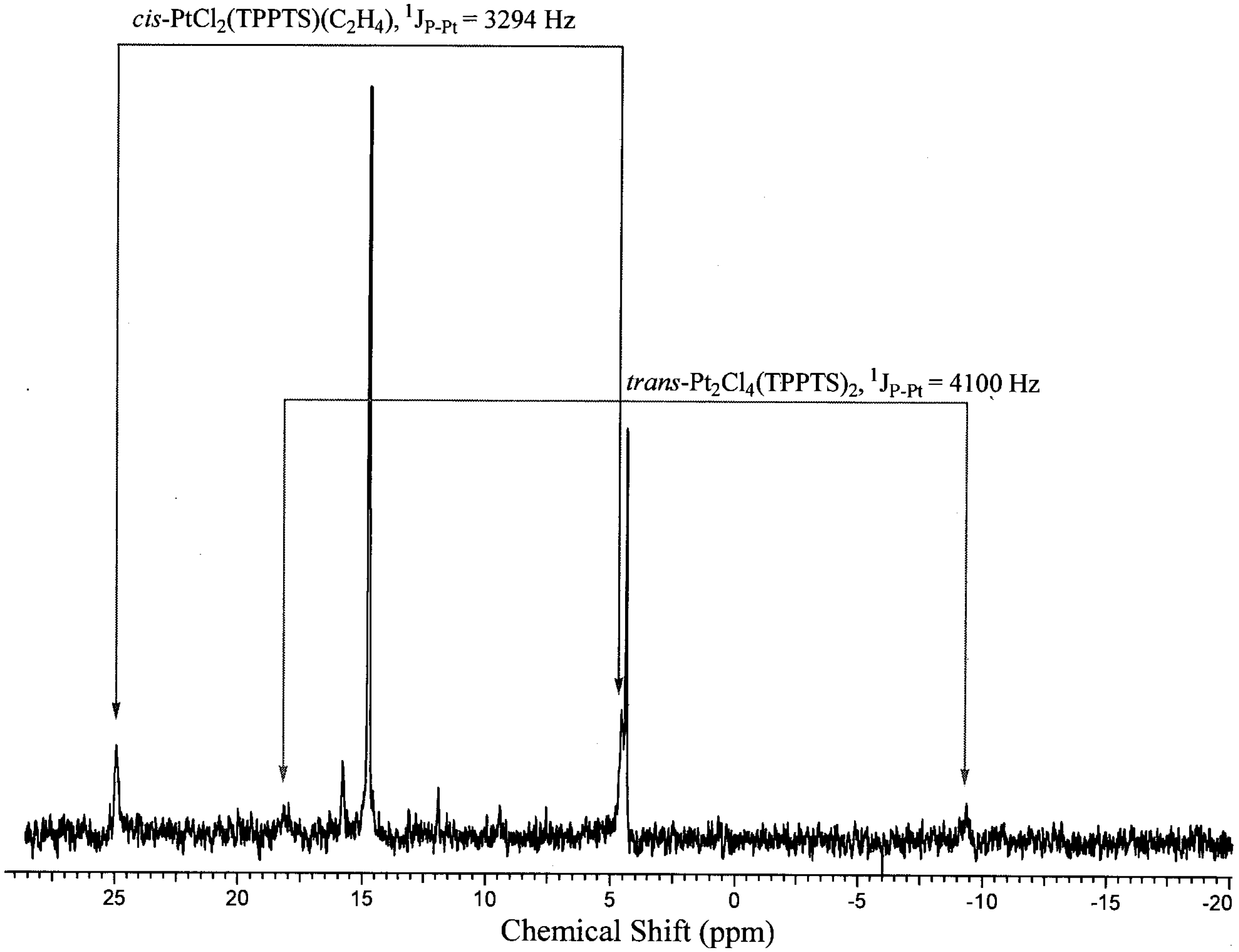

Figure 1. ^{31}P spectrum of *cis*-$PtCl_2(TPPTS)(C_2H_4)$ (14.7 ppm) showing some of the dimer $Pt_2(Cl)_2(TPPTS)_2(\mu\text{-}Cl)_2$ at 4.3 ppm.

significant are the doublet for ^{195}Pt indicating a single coordinated TPPTS and the magnitude of the J_{Pt-P} coupling.

The only phosphorus-containing contaminant is binuclear $Pt_2Cl_4(TPPTS)_2$, observed if sufficient reaction time under C_2H_4 pressure is not allowed.[11]

$$\textit{cis}\text{-}PtCl_2(TPPTS)(C_2H_4) \xrightarrow[-C_2H_4]{D_2O,\ >24\ h} \textit{trans}\text{-}Pt_2Cl_4(TPPTS)_2 \qquad (5)$$

Figure 1 shows the ^{31}P spectrum of a sample of *cis*-$PtCl_2(TPPTS)(C_2H_4)$ containing a small amount of the binuclear species.

Broadening in the ^1H resonance of bound C_2H_4 has been well studied,[19] including for the PPh_3 analogue,[20] *cis*-$PtCl_2(PPh_3)(C_2H_4)$, as rotation of the alkene about the platinum bond. Changing from PPh_3 to TPPTS has little effect on the broadening. We note that the aqueous solution of *cis*-$PtCl_2(TPPTS)(C_2H_4)$ is a bit sharper at 25 °C than the MeOH solution, suggesting more rapid rotation by the ethylene in water. The spectra are shown in Figure 2.

The NMR data in Table 1 were taken in CD_3OD, but little change occurs for aqueous solution. As an illustration, the proton spectrum in D_2O is shown in Figure 2; the ^{31}P spectrum in D_2O shows a small shift to about 13.2 ppm.

The ethylene complex is unusually stable in water between pH 0 and 9 (examined in 0.5 pH increments). Dissolving *cis*-$PtCl_2(TPPTS)(C_2H_4)$ in 20% HBF_4 showed no change in the ^1H and ^{31}P spectra. However, at pH 10.5 in D_2O in a sealed NMR tube the C_2H_4 was converted to ethanol and acetaldehyde in an approximate 1:1 ratio. Figure 3 presents ^1H NMR spectra at 30 min, 24 h, and 168 h. The ^1H NMR spectrum at 30 min shows some formation of C_2H_5OH (0.95 and 3.38 ppm) and the hydrate of acetaldehyde at 1.12 ppm.[5,21] The coordinated C_2H_4 resonance at 4.1 is still dominant, consistent with the ^{31}P spectrum, which shows mainly *cis*-$PtCl_2(TPPTS)(C_2H_4)$. After 24 h there is some C_2H_4 complex remaining; the C_2H_5OH has become clear with appropriate coupling and the acetaldehyde and hydrate (2.04 and 1.12 ppm) are both observed. In addition, resonances between 0 and 0.8 ppm are probably from $PtCH_2CH_2OH$ species, but lack clarity that would allow full assignment. The ^{31}P spectrum after 24 h shows the starting ethylene complex, a probable dinuclear product (at 1.8 ppm), and two other species. All four are of approximately the same intensity and singlets. After 168 h the ^{31}P NMR spectrum is dominated by the dimer and the ^1H NMR shows the resonances above 0.8 ppm have disappeared. Ethanol, acetaldehyde, and its hydrate

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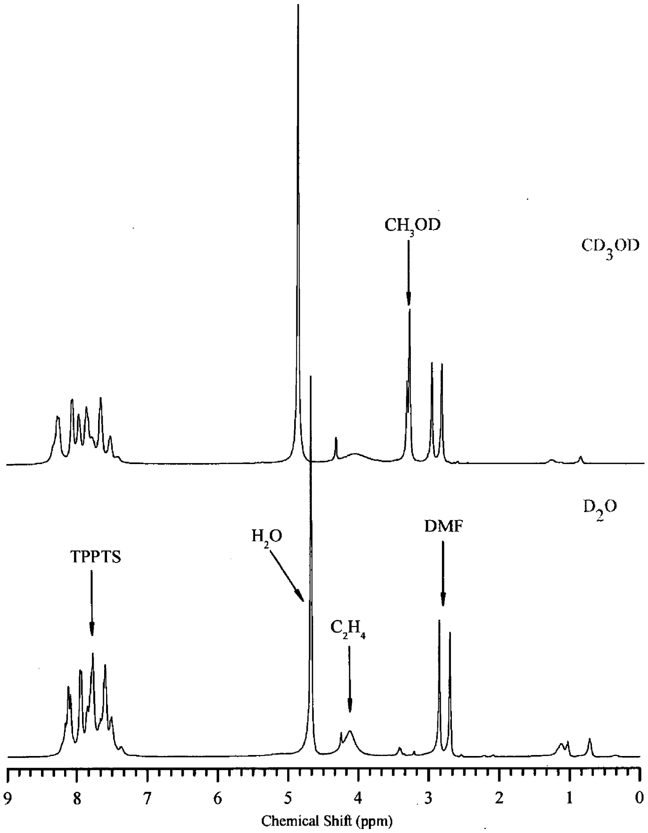

Figure 2. ^{1}H NMR spectra of *cis*-PtCl$_2$(TPPTS)(C$_2$H$_4$) showing the broadening from rotation in D$_2$O and in CD$_3$OD.

are still present, and a new resonance at 1.9 ppm may be acetic acid from oxidation of acetaldehyde.

Thus the reaction of coordinated C$_2$H$_4$ at pH 10.5 for *cis*-PtCl$_2$(TPPTS)(C$_2$H$_4$) in D$_2$O leads to acetaldehyde (and its hydrate) and ethanol. Acetaldehyde would be expected,[5] but ethanol through a hydration of C$_2$H$_4$ has not previously been observed on platinum. The NMR integration of the organic products shows deuterium incorporation in the methyl groups of ethanol and acetaldehyde to approximately the same extent, perhaps indicating a common intermediate; a β-hydroxy ethyl would be most likely. Usually deuterium incorporation into CH$_3$-CHO is not observed,[5,6a] but the reaction reported herein is quite slow and offers opportunities for deuterium incorporation. The primary platinum product (^{31}P at 1.8 ppm, $J_{\mathrm{Pt-P}} = 4256$ Hz) is not a known Pt(0) complex[22] and is most likely a hydroxo-bridged dimer[23] such as Pt$_2$(μ-OH)$_2$X$_2$L$_2$ where X = OH$^-$ or Cl$^-$, on the basis of the chemical shift and coupling constant. The very small amount of phosphine oxide observed in basic conditions excludes free TPPTS from a role.

Reaction of *cis*-PtCl$_2$(TPPTS)(C$_2$H$_4$) with NHEt$_2$ was examined in DMF at −35 °C.

$$\textit{cis}\text{-PtCl}_2\text{(TPPTS)(C}_2\text{H}_4\text{)} + \text{HNEt}_2 \xrightarrow{\text{DMF, }-35\ ^\circ\text{C}} \textit{cis}\text{-PtCl}_2\text{(TPPTS)(C}_2\text{H}_4\text{NHEt}_2\text{)} \quad (6)$$

The color changed from colorless to yellow. Addition of copious amounts of Et$_2$O resulted in a precipitate, which was collected and characterized as *cis*-PtCl$_2$(TPPTS)(C$_2$H$_4$NHEt$_2$). The yield was 60%. The diagnostic feature[11] is in the ^{1}H NMR (CD$_3$OD)

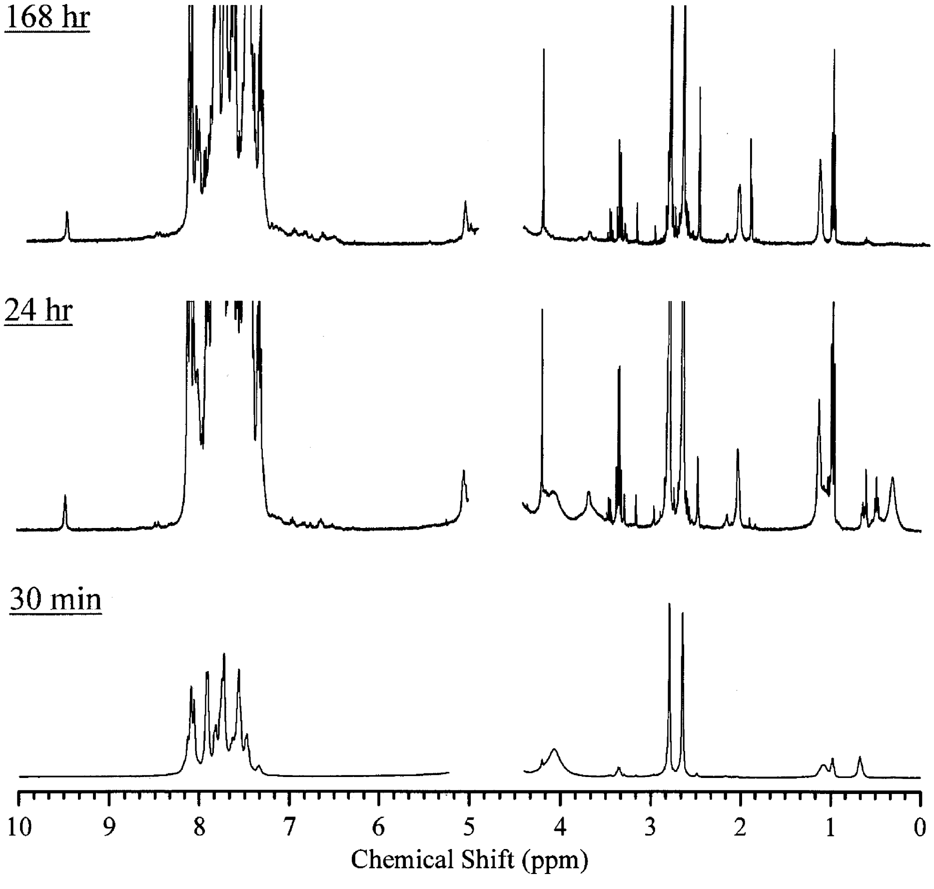

Figure 3. ^{1}H NMR spectra of *cis*-PtCl$_2$(TPPTS)(C$_2$H$_4$) at 30 min, 24 h, and 168 h in D$_2$O at pH 10.5. The break at ~5 ppm corresponds to residual protons in D$_2$O. The two resonances at ~3.5 and 3.7 ppm are from DMF; resonances at ~8 ppm are aromatic (TPPTS). The resonances growing in are discussed in the text.

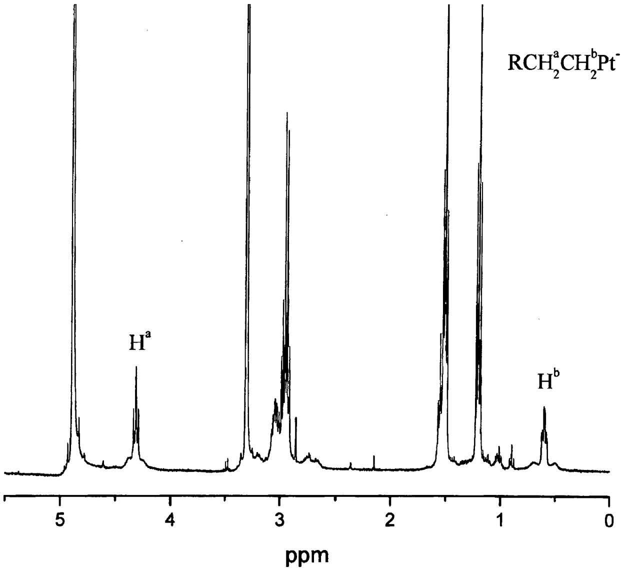

Figure 4. Partial ^1H NMR spectra of the amine reaction product, $PtCl_2(TPPTS)(CH^b{}_2CH^a{}_2NHEt_2)$. H^a and H^b show the distinctive ^{195}Pt satellites and chemical shifts.

for the two methylenes, both of which exhibit Pt−H coupling, at 0.51 ppm (CH_2 bound to Pt) and 4.3 ppm (CH_2 bound to $NHEt_3$) as shown in Figure 4. The ^1H NMR spectrum is nearly identical to that of *cis*-$PtCl_2(PPh_3)(CH_2CH_2NHEt_2)$[11] except for the presence of residual CD_3OD in the current spectrum. The ^{31}P spectrum shows a single resonance at 14.1 ppm, $J_{P-Pt} = 4383$ Hz, very similar to the PPh_3 analogue.[11]

A small resonance sometimes observed at 31 ppm is from the phosphine oxide, $OP(m\text{-}C_6H_4SO_3Na)_3$, formed under the basic conditions.

Conclusion

We have prepared a water-soluble platinum alkene complex, *cis*-$PtCl_2(TPPTS)(C_2H_4)$, characterized it by comparison to the PPh_3 analogue, demonstrated its stability in water from pH 0 to 9, shown that at pH 10.5 both hydration and formation of acetaldehyde occur, and demonstrated nucleophilic attack on the C_2H_4 by $NHEt_2$ leading to an isolable complex, *cis*-$PtCl_2(TPPTS)(CH_2CH_2NHEt_2)$.

Acknowledgment. R.S.P. acknowledges a Silbert Fellowship during his graduate studies.

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