Platinum-Catalyzed Wacker Oxidation of Alkenes Utilizing *cis*-$Pt(Cl)_2(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$)

Derrik S. Helfer and Jim D. Atwood*

Department of Chemistry, University at Buffalo, The State University of New York,
Buffalo, New York 14260

Received June 30, 2003

Reactions of alkenes (ethylene, propene, and 1-hexene) with water in the presence of *cis*-$Pt(Cl)_2(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) produces stoichiometrically the Wacker oxidation product (acetaldehyde, acetone, and 2-hexanone, respectively) and *trans*-$Pt(Cl)(H)(TPPTS)_2$. The presence of the phosphine ligands provides stability to the hydride complex such that decomposition to the metal is prevented. For C_2H_4 the final product is *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$. These reactions are fully consistent with the $PdCl_4^{2-}$ oxidation of alkenes. At higher temperatures, however, C_2H_4 is catalytically oxidized to CH_3CHO in a mechanism that appears to be different. At 95 °C, 90 turnovers are observed.

Introduction

Alkenes are among the most important feedstocks for chemical industry. This importance has resulted in many studies of transition-metal alkene complexes: structurally, theoretically, and mechanistically.[1−4] Most of these studies have centered on alkene complexes in organic solvents. Concerns for the environment create the need to minimize the use of organic solvents. For environmental benefits water is the preferred solvent, but there are relatively few studies of reactions of alkenes with transition-metal complexes in water. The Wacker process provides a notable exception.[3]

Acetaldehyde remains a major product of the US chemical industry, produced in 1 × 10^5 ton/year quantities.[5] While a number of approaches have been used, the Wacker process for oxidation of ethylene dominates. The Wacker process and interaction of C_2H_4 with $PdCl_4^{2-}$ have been frequently studied.[1−3,5−7] The following scheme is well accepted:

$$PdCl_4^{2-} + C_2H_4 \rightleftarrows PdCl_3(C_2H_4)^- + Cl^- \qquad (1)$$

$$PdCl_3(C_2H_4)^- + H_2O \rightleftarrows \textit{trans}\text{-}PdCl_2(H_2O)(C_2H_4) + Cl^- \qquad (2)$$

$$\textit{trans}\text{-}PdCl_2(H_2O)(C_2H_4) + H_2O \rightleftarrows \textit{trans}\text{-}PdCl_2(H_2O)(CH_2CH_2OH_2) \rightleftarrows \textit{trans}\text{-}PdCl_2(H_2O)(CH_2CH_2OH)^- + H^+ \qquad (3)$$

$$\textit{trans}\text{-}PdCl_2(H_2O)(CH_2CH_2OH)^- \xrightarrow{\beta\text{-elimination}} \textit{trans}\text{-}PdCl_2(H_2O)(CHMeOH)^- \qquad (4)$$

$$\textit{trans}\text{-}PdCl_2(H_2O)(CHMeOH)^- \xrightarrow{\beta\text{-elimination}} Pd(Cl_2)(H)(H_2O)^- + CH_3CHO \qquad (5)$$

$$PdCl_2(H)(H_2O)^- \rightarrow Pd + 2Cl^- + H^+ + H_2O \qquad (6)$$

The palladium then is oxidized to restart the reaction. The primary controversy concerned whether the H_2O/OH^- attacking the ethylene was external or was in the coordination sphere of the palladium (the hydroxypalladation step, reaction 3).

The key reaction for acetaldehyde formation from ethylene was reported in 1894 and was based on palladium. However, the palladium metal was not

---

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapters 10, 11, and 17, pp 149−155, 409−416, and references therein.

(2) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; Chapters 2−4, and references therein.

(3) Reference 2, Chapter 6.

(4) For platinum complexes: (a) *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, pp 519−680. (b) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science: Amsterdam, 1995; Vol. 9, pp 534−564.

(5) *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2002; Chapter 4.

(6) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; VCH: New York, 1997; pp 210−214, and references therein.

(7) (a) Wan, W. K.; Zaw, K.; Henry, P. M. *Organometallics* **1988**, *7*, 1677. (b) Gregor, N.; Zaw, K.; Henry, P. M. *Organometallics* **1984**, *3*, 1251. (c) Bäckvall, J. E.; Äkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411. (d) Stille, J. K.; Divakaruni, R. *J. Organomet. Chem.* **1979**, *169*, 239. (e) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*, D. Reidel: Dordrecht, The Netherlands, 1980; Chapter 2. (f) Saito, Y.; Shinoda, S. *J. Mol. Catal.* **1980**, *9*, 461. (g) Stille, J. K.; Divakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303. (h) Dedieu, A. *Catal. Met. Complexes* **1995**, *18*, 167. (i) Jira, R.; Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2002; Vol. 1, p 386.

10.1021/om030500b CCC: \$27.50
Publication on Web 04/07/2004

Table 1. Multinuclear NMR Characterization of Various Species in Water at Room Temperature

complex	$\delta(^{195}Pt)$[a]	$^1J_{Pt-P}$[b]	$\delta(^{31}P)$[a]	$^1J_{Pt-P}$[b]	$\delta(^1H)$ ($-CH_2CH_3$)[a]	$^2J_{Pt-H}$[b]	$\delta(^1H)$ ($-CH_2CH_3$)[a]
trans-$Pt(Cl)(C_2H_5)(TPPTS)_2$	−4703 (t)	3406	31.9 (s)	3406	0.58 (m)	90	0.12 (t) (65)
trans-$Pt(Cl)(C_2H_5)(PPh_3)_2$[11]			27.2 (s)	3340	0.7 (q)	93	0.2 (t) (61)
trans-$Pt(H_2O)(C_2H_5)(TPPTS)_2^+$	−4497 (t)	3474	32.5 (s)	3474	0.75 (m)		−0.14 (t)
							0.57 (br, CH_β)[d]
trans-$Pt(Cl)(n\text{-}C_3H_7)(TPPTS)_2$			32.0 (s)	3369	0.49 (br, CH_α)[d]		−0.30 (t, CH_γ)[d]
trans-$Pt(H_2O)(n\text{-}C_3H_7)(TPPTS)_2^+$			32.5 (s)				
$Pt(C_2H_5)(TPPTS)_3^+$			27.0 (d)	3253 (19)[c]	0.98 (br)		0.03 (br)
			18.7 (t)	1652			
$Pt(C_2H_5)(PPh_3)_3^+$ [12]			25.7 (d)	3140 (19)[c]	1.21 (br)		
			18.7 (t)	1674			
$Pt(C_2H_4)_2(TPPTS)$	−5500 (d)	3391	26.9 (s)	3391	2.46 (s, C_2H_4)	58	
$Pt(C_2H_4)_2(PPh_3)$[13]			25 (s)	3425	2.7 (s, C_2H_4)	57	
$Pt(C_2H_4)(TPPTS)_2$	−5040 (t)	3670	34.9 (s)	3670	2.13 (s, C_2H_4)	60	
$Pt(C_2H_4)(PPh_3)_2$[14]			32.5 (s)	3694	2.15 (s, C_2H_4)	62	
trans-$Pt(OH)(C_2H_5)(TPPTS)_2$			32.0 (s)	3465	0.30 (q)		−0.13 (t)
cis-$Pt(OH)(C_2H_5)(TPPTS)_2$	−4491 (dd)	1538	29.5 (d)	1538 (9)[c]	0.96 (m)		0.55 (m)
		4279	18.1 (d)	4279			

[a] Chemical shifts given in ppm. [b] Coupling constants given in Hz. [c] Numbers in parentheses correspond to $^2J_{P-P}$, given in Hz. [d] Recorded on a 500 MHz NMR spectrometer.

cleanly reoxidized by O_2 to a soluble complex and the process was not developed until the 1950s, adding $CuCl_2$ to oxidize Pd to $PdCl_4^{2-}$. The role of Cl^- is to stabilize and solubilize the metal complexes. A number of studies have examined the effect of Cl^- on the oxidation of alkenes and the incorporation of chloride into the organic products. The rate law shows an inverse second-order dependence on $[Cl^-]$, attributed to two Cl^- ligand replacements.[7]

The Wacker system does not allow identification of intermediates; therefore, the detailed mechanism is based on kinetics, products, and labeling studies. Use of other alkenes produces ketone products from Markovnikov addition of H_2O in eq 3.[1−3,5−7]

Other reactions of alkenes in water have not been as well studied.[8,9] Hydroformylation of alkenes occurs in water and is commercialized for propene in a mechanism presumed to be very similar to hydroformylation by $Rh(CO)(H)L_3$ in organic solvents.[8] Hydrogenation of alkenes occurs in water, but again the mechanism accepted for organic solvents is presumed to pertain.[9]

Given the rapid attack of water on alkenes coordinated to Pd(II) in the Wacker process and the lack of such interaction by Rh(I) and other complexes in hydroformylation and hydrogenation reactions, further study of the interaction of alkenes with metal complexes in water is imperative. Platinum complexes of the water-soluble phosphine ligand TPPTS[9] form the basis of this paper.

Results and Discussion

Stoichiometric Reactions. Reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with ethylene in water at room temperature resulted in the formation of *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ (88%) and *trans*-$Pt(H_2O)(C_2H_5)(TPPTS)_2^+$ (12%), as determined by ^{31}P NMR integration. The aqua species results from chloride dissociation. Evidence for this was shown by the addition of a small crystal of $AgNO_3$ to a solution which consisted primarily of *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$. AgCl immediately precipitated, and the resonances for the aqua species grew. The ethyl aqua complex was the main product when *cis*-$Pt(H_2O)_2(TPPTS)_2^{2+}$ was reacted with ethylene under analogous conditions. Chloride dissociation was also seen upon dissolution of *trans*-$Pt(Cl)(CH_3)(TPPTS)_2$ in water.[10] This dissociation occurs due to the large trans effect exhibited by both the methyl and ethyl moieties. Thus, the Pt−Cl bond, which lies trans to the alkyl in the square plane, becomes elongated and more easily substituted.

The Pt−P coupling constant ($^1J_{Pt-P}$) for *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ was found to be 3406 Hz. Since TPPTS and PPh_3 have been found to be similar electronically, comparison to the PPh_3 analogue is shown in Table 1. J_{Pt-P} is a useful tool in determining the geometry and bond strength for Pt^{II} species. For example, replacement of the chloride with a second ethyl moiety changes not only the bond strength but also the geometry of the molecule. In *cis*-$Pt(C_2H_5)_2(TPPTS)_2$, synthesized by Komiya et al.,[15] this value drops to 1677 Hz, indicating the strong trans effect of the ethyl moiety on the Pt−P bond. Addition of excess phosphine to a solution of *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ generates $Pt(C_2H_5)(TPPTS)_3^+$. In this case, two phosphines are trans to each other, while the third lies trans to the ethyl moiety. The Pt−P coupling constant of the two trans phosphines was calculated to be 3253 Hz, while the value for the phosphine trans to the ethyl was 1652 Hz.

Along with the formation of the Pt−ethyl species (Figure 1 shows the ^1H NMR spectrum of the ethyl

---

(8) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177−186.

(9) (a) Joó, F.; Kathó, A. *J. Mol. Catal. A* **1997**, *116*, 3. (b) Papdogianakis, G.; Sheldon, R. A. *New J. Chem.* **1996**, *20*, 175. (c) Roundhill, D. M. *Adv. Organomet. Chem.* **1995**, *38*, 155. (d) Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, *24*, 43. (e) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219. (f) Joó, F.; Tóth, Z. *J. Mol. Catal.* **1980**, *8*, 369. (g) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (h) Sheldon, R. A. *Chem. Ind.* **1997**, *6*, 12. (i) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997; pp 115−160. (j) Hanson, B. E. *Coord. Chem. Rev.* **1999**, *185*, 795.

(10) Lucey, D. W.; Helfer, D. S.; Atwood, J. D. *Organometallics* **2003**, *22*, 826.

(11) Bogdashkina, V. I.; Permin, A. B.; Petrosyan, V. S.; Reutov, O. A. *Dokl. Chem.* **1983**, *266*, 331.

(12) Pregosin, P. S.; Favez, R.; Roulet, R.; Boschi, T.; Michelin, R. A.; Ros, R. *Inorg. Chim. Acta* **1980**, *45*, L7.

(13) Harrison, N. C.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1337.

(14) (a) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464. (b) Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073.

(15) Komiya, S.; Ikuine, M.; Komine, N.; Hirano, M. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 183.

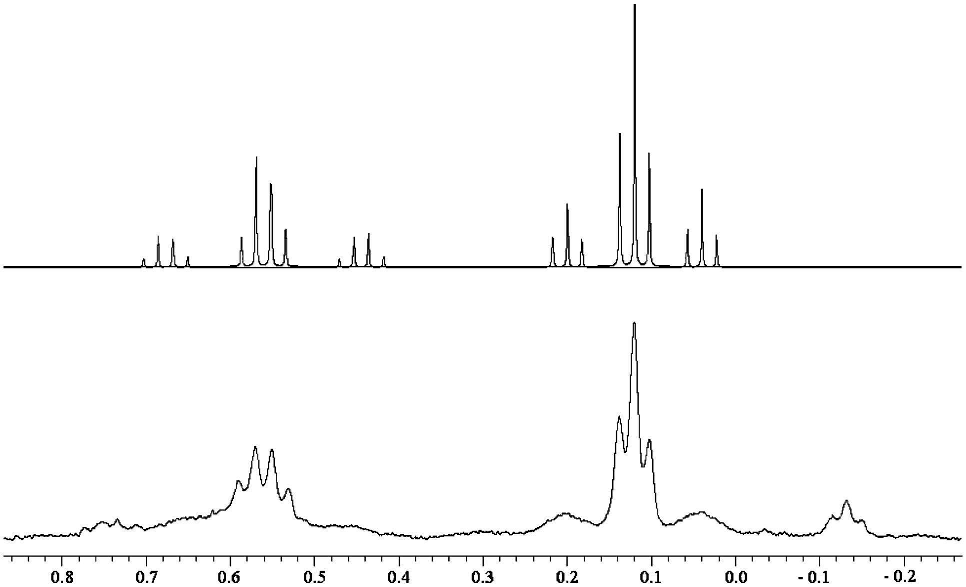
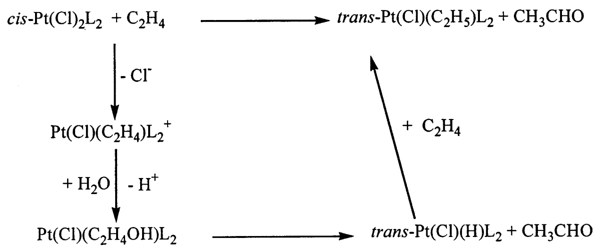


Figure 1. Simulated (top) and actual (bottom) ^{1}H NMR spectra of the ethyl resonance of *trans*-Pt(Cl)(C_2H_5)(TPPTS)$_2$, showing the location of the Pt satellites. The triplet at −0.14 ppm and multiplet at 0.75 ppm are from *trans*-Pt(H_2O)-(C_2H_5)(TPPTS)$_2^+$.

group compared to a simulated spectrum), we observed conversion of ethylene to acetaldehyde (δ 2.04 (d, CH_3-CHO, 3H) and 9.48 (br, CH_3C*H*O, 1H)), as determined by ^{1}H NMR. In water, acetaldehyde is found in a 0.8: 1.0 ratio with its hydrate (δ 1.12 (d, CH_3CH(OH)$_2$, 3H) and 5.04 (q, CH_3C*H*(OH)$_2$, 1H)) at 25 °C.[16] We also observed traces of acetic acid (δ 1.89 (s, CH_3COOH)), most likely due to autoxidation of acetaldehyde with oxygen.[17] The amount of acetaldehyde produced was determined by comparing the ^{1}H NMR integration of acetaldehyde (including the hydrate and acetic acid) against the aromatic region (7−8 ppm) of the spectrum. As will be discussed, the amount of the organic product is stoichiometric with the amount of *trans*-Pt(Cl)(H)-(TPPTS)$_2$ produced. Since an excess of ethylene is present, insertion occurs to give the ethyl species.

The pH of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ upon dissolution in triply distilled water was ~3. After the reaction with ethylene, the pH was ~2, indicating proton evolution. Reasons for this decrease in pH will be discussed in the next section. When the beginning solution was adjusted to a pH of ~0.6 by addition of concentrated HBF_4, the rate of the reaction decreased sharply. Only a trace of acetaldehyde was produced. In the $PdCl_4^{2-}$-catalyzed Wacker oxidation of ethylene, proton inhibition was noted,[18] while reaction with cyclohexene proceeds without proton inhibition.[18a] Reaction under basic conditions will be discussed in a later section.



(7)

The reaction of ethylene with *cis*-Pt(Cl)$_2$(TPPTS)$_2$ probably proceeds according to the scheme (L = TPPTS)-The reaction is similar to the $PdCl_4^{2-}$-catalyzed Wacker-type chemistry.[7] The first step would involve coordination of the ethylene to the metal center via chloride dissociation. Next, attack by a hydroxide or water would produce the hydroxyethyl complex. Numerous theoretical studies have been utilized in discerning the exact nature of this step: in particular, whether a cis or trans attack occurs by either a coordinated hydroxide or a hydroxide from the solvent.[7,19] It has been generally accepted that the attack is indeed trans.[19a] Siegbahn has shown that this mode is favorable when chains of water molecules are present in the coordination sphere.[19b] Henry et al. have proposed that this step is rate-limiting, in the $PdCl_4^{2-}$-catalyzed case, and involves intramolecular attack of a coordinated solvent or hydroxide on the bound ethylene to afford the hydroxyethyl species.[7e] Calculations performed by Nelson showed that the rate-determining step was nucleophilic, which supports the mechanism proposed by Henry.[19c]

This step would then be followed by numerous β-hydrogen transfers/eliminations in order to eliminate acetaldehyde and form a Pt^{II}−H species, although Pd(0) is generated when $PdCl_4^{2-}$ is used. Even Zeise's salt is reported to decompose by the equation[7e]

$$[PtCl_3(C_2H_4)]^- + H_2O \rightarrow CH_3CHO + Pt^0 + 2HCl + Cl^- \quad (8)$$

Therefore, the presence of the phosphine ligands stabilizes the Pt−H complex. Such platinum hydride complexes containing phosphorus ligands are known to be very stable in solution.[20] As can be seen from reaction

---

(16) Schuchmann, M. N.; von Sonntag, C. *J. Am. Chem. Soc.* **1988**, *110*(17), 5698.

(17) Fessenden, R. J.; Fessenden, J. S.; Logue, M. W. *Organic Chemistry*, 6th ed.; Brooks/Cole: New York, 1998; p 259.

(18) (a) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*(16), 3246. (b) Vargaftik, M. N.; Moiseev, I. I.; Syrkin, Y. K. *Dokl. Phys. Chem.* **1962**, *147*(1−6), 804.

(19) (a) Kragten, D. D.; van Santen, R. A.; Lerou, J. J. *J. Phys. Chem. A* **1999**, *103*, 80. (b) Siegbahn, P. E. M. *J. Phys. Chem.* **1996**, *100*, 14672. (c) Nelson, D. J.; Li, R.; Brammer, C. *J. Am. Chem. Soc.* **2001**, *123*, 1564.

(20) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.

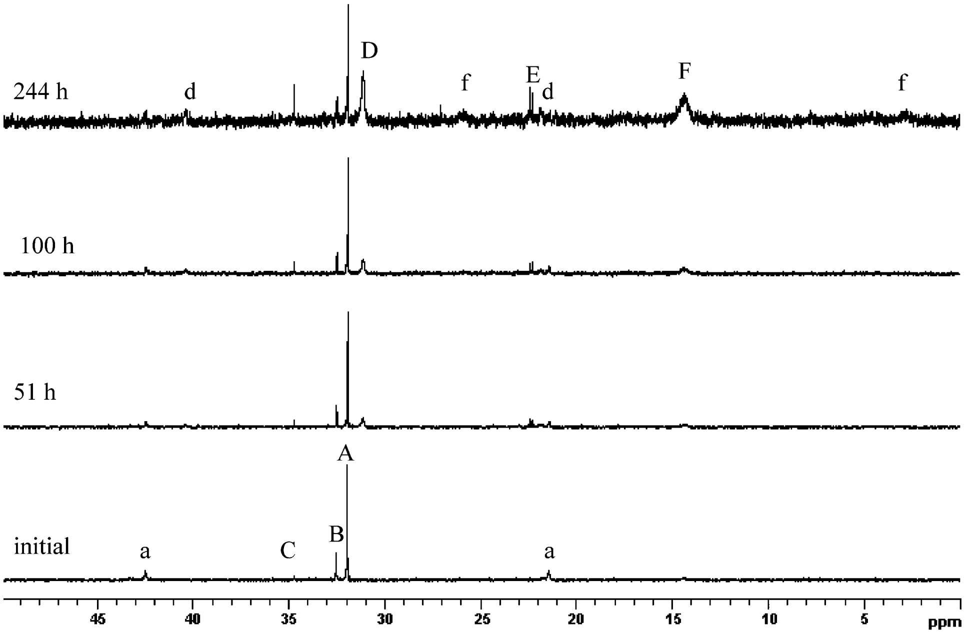
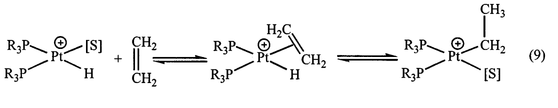


Figure 2. Array of ^{31}P NMR spectra showing the stability of *trans*-Pt(Cl)(C_2H_5)(TPPTS)$_2$ (A), in solution, over time. Initially 82% of A, 16% of *trans*-Pt(H_2O)(C_2H_5)(TPPTS)$_2^+$ (B), and 2% of OTPPTS (C) were present. After 51 h, the formation of *trans*-Pt(Cl)(H)(TPPTS)$_2$ (D), Pt(H)(TPPTS)$_3^+$ (E), and *cis*-Pt(Cl)$_2$(TPPTS)$_2$, (F) were seen. These products continued to become more abundant after 100 h. After 244 h, equal amounts of F (41%) and the two hydride species D and E (40%) were present along with 12% A, 4% B, and 3% C. Lower case letters represent Pt satellites.

7, acetaldehyde and *trans*-Pt(Cl)(H)(TPPTS)$_2$ are formed stoichiometrically. Separate deuterium incorporation experiments utilizing D_2O as the solvent and C_2D_4 as the substrate produced CH_3CHO and CD_3CDO, respectively. This is consistent with the mechanism proposed for $PdCl_4^{2-}$-catalyzed Wacker oxidation, in which the ethylene protons, and not the solvent protons, are incorporated into the acetaldehyde.[7e]

Insertion of ethylene into the Pt−H bond produces the ethyl complex. Reaction 7 also accounts for 1 equiv of H^+ produced, consistent with the observed pH change. A similar mechanism was suggested by Sen et al. for the reaction of K_2PtCl_4 with ethylene in water, in which acetaldehyde was produced along with formation of [Pt(μ-Cl)(C_2H_5)(C_2H_4)]$_2$.[21] Addition of 1,10-phenanthroline (N−N) caused splitting of the dimer and formation of (N−N)Pt(Cl)(C_2H_5) and ethylene. They too proposed the formation of a Pt^{II}−H species and generation of an ethyl moiety. Numerous computational studies have been performed on olefin insertion into Pt^{II}−H bonds.[22] The generally accepted insertion occurs according to reaction 9.[22a] According to reaction 9, *cis*-Pt(Cl)(C_2H_5)(TPPTS)$_2$



(9)

would initially be formed. Formation of the trans isomer in reaction 7 indicates isomerization, probably through a dissociative mechanism in which a 14-electron, T-shaped cationic intermediate forms upon dissociation, as proposed by Romeo et al.[23] Similar behavior was seen in the protonolysis of *cis*-Pt(CH_3)$_2$(TPPTS)$_2$, in which *cis*-Pt(Cl)(CH_3)(TPPTS)$_2$ initially forms but undergoes isomerization to the more stable trans isomer.[10]

Various pressures of ethylene were employed, up to 54 atm, and we found that pressures above 14 atm at room temperature gave optimal yields of both acetaldehyde and *trans*-Pt(Cl)(C_2H_5)(TPPTS)$_2$; therefore, we employed a pressure of 31 atm. The reaction of K_2PtCl_4 and ethylene, done by Sen et al., was under a pressure of 54 atm.[16] In the commercial Wacker process, an ethylene pressure of 7−13 atm is required, along with reaction temperatures of 100−110 °C.[7e] It is not uncommon for increased pressures of ethylene to be required, especially when considering insertion of ethylene into a Pt−H bond. Chatt and Shaw reacted *trans*-Pt(Cl)(H)(PEt$_3$)$_2$ with an ethylene pressure of 40 atm at 95 °C to afford a 25% yield of *trans*-Pt(Cl)(C_2H_5)(PEt$_3$)$_2$.[20] Chatt et al. were able to achieve a quantitative yield of *trans*-Pt(Cl)(C_2H_5)(PEt$_3$)$_2$ by reacting the hydride species at 80 °C/192 atm.[24]

The stability of *trans*-Pt(Cl)(C_2H_5)(TPPTS)$_2$ was investigated by allowing one of the reaction mixtures, which contained ~90% of this complex, to stand over time in the absence of ethylene. NMR spectra were recorded periodically to monitor the changes in composition (Figure 2). This complex decomposes into *trans*-Pt(Cl)(H)(TPPTS)$_2$ (^{31}P, δ 31.0 (s), $^1J_{\mathrm{Pt-P}} = 3038$ Hz; ^{1}H, δ −16.6 (t), $^2J_{\mathrm{P-H}} = 19$ Hz, $^1J_{\mathrm{Pt-H}} = 1189$ Hz) due to elimination of ethylene. This hydride complex is unstable in aqueous solution and ultimately forms the

---

(21) Basickes, N.; Hutson, A. C.; Sen, A.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 4116.

(22) (a) Coussens, B. B.; Buda, F.; Oevering, H.; Meier, R. J. *Organometallics* **1998**, *17*, 795. (b) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. (c) Recha, W. R.; De Almeida, W. B. *Organometallics* **1998**, *17*, 1961. (d) Sakaki, S.; Ogawa, M.; Musaski, Y.; Arai, T. *J. Am. Chem. Soc.* **1994**, *116*, 7258. (e) Sakaki, S.; Kato, H.; Kanai, H.; Tarama, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 813.

(23) Romeo, R.; Plutino, M. R.; Elding, L. J. *Inorg. Chem.* **1997**, *36*, 5909.

(24) Chatt, J.; Coffey, R. S.; Gough, A.; Thompson, D. T. *J. Chem. Soc.* **1968**, 190.

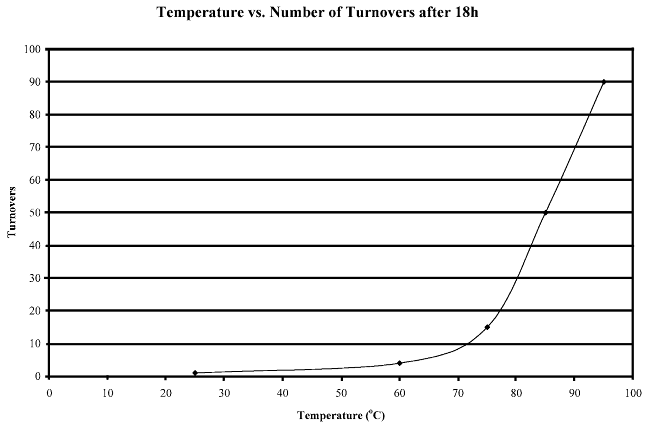


Figure 3. Graph of temperature (in °C) versus turnovers calculated after 18 h from the reaction of *cis*-Pt(Cl)$_2$-(TPPTS)$_2$ and ethylene at the specified temperatures.

stable hydride Pt(H)(TPPTS)$_3{}^+$.[25] This instability of a bis-phosphine hydride complex in an aqueous environment was also noted by Marsella et al., observing that a pure sample of *trans*-Pt(Cl)(H)(PMe$_3$)$_2$ formed the cationic tris complex upon dissolution in water.[26] Whitesides et al. proposed that the rate-limiting step in the elimination of C_2H_4 from an ethyl complex occurs in formation of a five-coordinate intermediate:[27]

$$L_2Pt(Cl)(C_2H_5) \rightarrow [L_2Pt(H)(Cl)(C_2H_4)] \rightarrow L_2Pt(H)(Cl) + C_2H_4 \quad (10)$$

We also observed the formation of ethane (δ 0.69 (s, $C_2\mathit{H}_6$)) and regeneration of *cis*-Pt(Cl)$_2$(TPPTS)$_2$, which is likely due to protonolysis of *trans*-Pt(Cl)(C$_2$H$_5$)-(TPPTS)$_2$. As shown by the spectra in Figure 2, the rate of protonolysis is quite slow from the trans complex, analogous to what we found for *trans*-Pt(Cl)(CH$_3$)-(TPPTS)$_2$.[10] Also, the rate of β-elimination is similar to that of the protonolysis, since nearly equal quantities of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ and the hydride species are present throughout the decomposition of *trans*-Pt(Cl)-(C$_2$H$_5$)(TPPTS)$_2$.

Catalytic Reactions. When the reaction mixture of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ and ethylene was heated, catalytic formation of acetaldehyde was seen (Figure 3). At a temperature of 60 °C, a total of five turnovers (based on ^{1}H NMR integration) was seen after 18 h. However, as the temperature was subsequently increased to 75 °C, the turnover number increased to 15 after the same amount of time. The most significant increase was seen when the reaction temperature was 95 °C, in which 90 turnovers resulted. *trans*-Pt(Cl)(C$_2$H$_5$)(TPPTS)$_2$ was observed as the main product by ^{31}P NMR, up to 75 °C. However, above this temperature, the resulting solution was bright yellow and contained a black precipitate. The pH for these catalytic reactions is the same as for the stoichiometric reaction (reaction 7). Thus, the additional protons must be involved in the reaction. The two most probable reactions would be protonolysis of the platinum hydride or platinum ethyl complex:

$$\textit{trans}\text{-}Pt(Cl)(H)(TPPTS)_2 + H^+ \rightarrow Pt(Cl)(H_2O)(TPPTS)_2{}^+ + H_2 \quad (11)$$

$$\textit{trans}\text{-}Pt(Cl)(C_2H_5)(TPPTS)_2 + H^+ \rightarrow Pt(Cl)(H_2O)(TPPTS)_2{}^+ + C_2H_6 \quad (12)$$

Therefore, to determine which pathway was occurring, analysis of the resulting gas mixture from the reaction of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ with ethylene at 95 °C was accomplished by bubbling the gas through d_6-benzene for 5 min. Analysis of this solution by ^{1}H NMR revealed the following: δ 9.11 (q, CH$_3$C*H*O), 5.22 (s, C$_2$*H*$_4$), 1.34 (d, C*H*$_3$CHO), and 0.78 (s, C$_2$*H*$_6$). The solution was analyzed by ^{13}C NMR as well, in which the following signals were seen: δ 196.9 (s, CH$_3$*C*HO), 122.1 (s, *C*$_2$H$_4$), 29.4 (s, *C*H$_3$CHO), and 6.1 (s, *C*$_2$H$_6$). The chemical shifts are consistent with the literature.[28] Analysis of just the ethylene gas showed no signal for the presence of ethane by ^{1}H NMR. We also bubbled natural gas from a gas jet through benzene for 5 min and analyzed the resulting solution by ^{1}H NMR. The following resonances were seen: δ 0.78 (s, C$_2$*H*$_6$) and 0.14 (s, C*H*$_4$). Therefore, on the basis of these results, we are confident that the latter of the two pathways (reaction 12) is occurring.

^{31}P NMR of the yellow solution formed at 95 °C showed a sharp singlet at δ 0.06 ppm, with the absence of ^{195}Pt$-^{31}$P coupling. Analysis of the sample by ^{13}C-{^{1}H} NMR showed only singlets in the aromatic region; thus, no ^{13}C$-^{31}$P coupling was seen. Therefore, on the basis of these results, we proposed that the product seen in the ^{31}P NMR was phosphate. This was proved by addition of a few crystals of NaH$_2$PO$_4$ to the yellow solution, causing the resonance to grow. To form phosphate from TPPTS, the phenyl rings of the phosphine must be cleaved; interpretation of the aromatic region of the ^{1}H NMR was difficult, due to the presence of numerous overlapping signals. The stability of TPPTS under the above conditions was determined by reacting a solution of TPPTS with a few drops of acetaldehyde under ethylene at 95 °C. The resulting solution was colorless, no reaction with C$_2$H$_4$ was observed, and the ^{31}P NMR showed a free TPPTS resonance and a small broad resonance at δ 24.0 ppm. Thus, the P$-$C cleavage must be metal catalyzed. This type of behavior is not uncommon in the literature. Kikukawa et al. demonstrated that Pd(OAc)$_2$ could cleave phosphine bonds according to the scheme[29]

$$Ph_3P + Pd(OAc)_2 + CH_2{=}CHPh \xrightarrow[48\ h]{\text{room temp}} \xrightarrow{\text{(i) OH}^-} \xrightarrow{\text{(ii) H}^+} PhCH{=}CHPh + PhCH{=}CHOAc\ (\text{trace}) + Ph_2P(O)OH + PhP(O)(OH)_2 + H_3PO_4 + Ph_3P{=}O \quad (13)$$

---

[25] Helfer, D. S.; Atwood, J. D. *Organometallics* **2002**, *21*, 250.

[26] Ramprasad, D.; Yue, H. J.; Marsella, J. A. *Inorg. Chem.* **1988**, *27*, 3151.

[27] (a) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550. (b) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *74*, 550.

[28] (a) Sadykov, R. A.; Shishlov, N. M. *J. Organomet. Chem.* **1989**, *369*, 1. (b) Loaiza, A.; Brochardt, D.; Zaera, F. *Spectrochim. Acta, Part A* **1997**, *53*, 2481.

[29] Kikukawa, K.; Matsuda, T. *J. Organomet. Chem.* **1982**, *235*, 243.

Under hydroformylation conditions, Rh, Co, and Ru were also shown to cause the cleavage of P−C bonds in para-substituted triphenylphosphines.[30]

Another set of reactions was run at 95 °C, with 3.5 times the amount of the *cis*-$Pt(Cl)_2(TPPTS)_2$ utilized in order to increase the concentration of the species in solution. The yellow solution was isolated from the black precipitate by gravity filtration. To the yellow filtrate was added excess ethanol, which caused precipitation of a yellow solid. A rotary evaporator was used to remove the solvent. The resulting solid was redissolved in a minimum of D_2O, and an attempt was made to take a ^{195}Pt NMR spectrum. However, repeated attempts with various samples showed no signal. It is possible that various Pt compounds are present and their abundances are just too small to be detected by this method. Pt was proven to be present by reacting the isolated yellow material with ethylene under the same conditions as stated above. The resulting solution from the autoclave again contained a black precipitate along with a yellow solution. A small amount of acetaldehyde was seen in the ^1H NMR spectrum of the yellow solution. ^{31}P NMR analysis again showed only a sharp resonance at δ 0.06 ppm. On the basis of these results and those observed previously, the formation of acetaldehyde is due to reaction of ethylene with the solvated Pt in solution. Since no phosphine is present to stabilize the metal center, Pt black or a cluster type species ultimately forms. Ethane was once again detected in the vent gas from the autoclave in a manner similar to that previously described. Also, to account for the reaction of ethylene with the solvated Pt to produce the black precipitate, a solution of the yellow solid was heated under argon at 95 °C for 18 h. After the allotted time, no precipitate was present.

We also attempted to analyze the black precipitate from the reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ and ethylene at 95 °C. This product was isolated from the yellow solution by centrifuge and washed with distilled water. Analysis proved difficult, since the solid was not soluble in any common organic solvent and the amounts collected were too small for elemental analysis. Therefore, we decided to analyze the solid by X-ray photoelectron spectroscopy (XPS).[31] Analysis by XPS showed an average of 7.6% Pt with an observed shift of the Pt $4f_{7/2}$ ejection of 70.1 eV. The literature value for Pt(s) was found to be 70.9 eV.[32] Analysis of *cis*-$Pt(Cl)_2(TPPTS)_2$ by the same method showed a Pt concentration of 0.9% with an observed shift of 72.0 eV. This shift is also comparable to the value for $Pt(Cl)_2(PPh_3)_2$ of 72.1 eV.[32] Therefore, on the basis of these results, we believe that the black solid is Pt. Reaction of this compound with ethylene at 95 °C in water showed no further oxidation of the substrate.

Reactions Under Basic Conditions. Reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with ethylene under basic conditions provides different products. Addition of NaOH to a solution of the starting complex immediately gives $[Pt(\mu\text{-}OH)(TPPTS)_2]_2^{2+}$ (85%) and OTPPTS (15%) above a pH of 10, as determined by ^{31}P NMR integration.[33] When this mixture was reacted with ethylene for 18 h at room temperature, we observed formation of $Pt(C_2H_4)_2(TPPTS)$ (25%) and increased formation of OTPPTS (30%). Multinuclear NMR characterization of the former is in agreement with the organic analogue $Pt(C_2H_4)_2(PPh_3)$,[13] as shown in Table 1. Reaction for longer periods of time (up to 48 h) caused further oxidation of the ligand and only small increases in formation of the Pt^0 complex. To help provide support for the formation of this complex, $Pt(Cl)(TPPTS)_3^+$ was reacted with ethylene under basic conditions. The solution chemistry of this species is not as straightforward as that for the corresponding bis-phosphine complex. When the pH is increased above 13, a red solution is produced along with OTPPTS (25%), $Pt(TPPTS)_3$ (25%), and $[Pt(\mu\text{-}OH)(TPPTS)_2]_2^{2+}$ (50%). Interestingly, none of the species present form a red solution. At a pH of around 12, a similar spectrum is produced, but the solution is yellow. When this yellow solution reacted with ethylene at room temperature for 18 h, $Pt(C_2H_4)(TPPTS)_2$ was produced in approximately 30% yield, along with a trace of $Pt(C_2H_4)_2(TPPTS)$. We have previously characterized $Pt(C_2H_4)(TPPTS)_2$;[25] the NMR data for this species and its comparison to $Pt(C_2H_4)(PPh_3)_2$ are shown in Table 1.

In a recent communication, we detailed the interconversion of $Pt^{II}(H)(TPPTS)_3^+$ and $Pt^0(TPPTS)_3$ as a function of pH.[25] Therefore, we attempted to test whether *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ and $Pt(C_2H_4)(TPPTS)_2$ could be similarly interconverted. When a solution containing $Pt(C_2H_4)(TPPTS)_2$ (produced from reaction of $Pt(Cl)(TPPTS)_3^+$ described above) was made acidic by addition of HBF_4, *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ was produced in near-quantitative yield, along with *cis*-$Pt(Cl)_2(TPPTS)_2$. The presence of ethane was seen in the ^1H NMR from some protonolysis of the ethyl moiety and formation of the dichloro complex. The chloride product was formed, as opposed to the *aquo*, due to the solvated chloride that remained in solution. A mechanism proposed by Whitesides et al. details this transformation, as shown in reaction 14.[34]

$$L_2PtC_2H_4 \xrightleftharpoons{+H^+} L_2Pt(H)(C_2H_4)^+ \rightleftharpoons L_2Pt(C_2H_5)^+ \xrightleftharpoons{+X^-} L_2Pt(X)(C_2H_5) \xrightarrow{HX} L_2PtX_2 + C_2H_6 \qquad (14)$$

From this mechanism, an equilibrium should exist between the ethyl species and the ethylene; however, reactions of *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ were inconsis-

---

(30) Sakakura, T.; Kobayashi, T.-A.; Hayashi, T.; Kawabata, Y.; Tanaka, M.; Ogata, I. *J. Organomet. Chem.* **1984**, *267*, 171.

(31) X-ray photoelectron spectroscopy was done on a Physical Electronics Model (Perkin-Elmer) 5300 X-ray photoelectron spectrometer. For XPS measurements, X-rays were generated with Mg targets. Ejected electrons are analyzed with a hemispherical analyzer capable of a resolution of 0.1 eV. Samples can be analyzed in a range of angles relative to the analyzer from 10_θ to 90_θ to provide varying degrees of surface sensitivity. Analysis depths of 1 to 20 nm are possible but are sample dependent. Data analysis was performed on a Pentium II 350 MHz computer which was connected to the instrument with an RBD manufactured interfaced control. The RBD software (AugerScan) can provide the user with basic atomic surface concentrations, chemical information from peak shifts due to the chemical environment, and depth information by angle resolved experiments of ion gun spattering. The data were charge referenced to the aliphatic (C1s) ejection peak of 284.6 eV.

(32) Wagner, C. D.; Riggs, R. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of Electron Spectroscopy*; Perkin-Elmer Corp., Physical Electronics: Eden Prairie, MN, 1979; p 152.

(33) Francisco, L. W.; Moreno, D. A.; Atwood, J. D. *Organometallics* **2001**, *20*, 4232.

(34) Foley, P.; Whitesides, G. M. *Inorg. Chem.* **1980**, *19*, 1402.

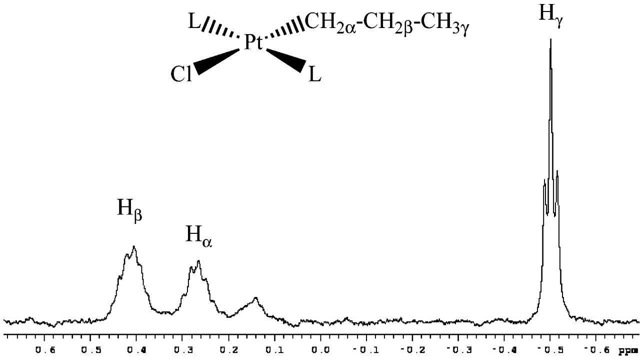


Figure 4. ^1H NMR spectrum (alkyl region) of the solution resulting from the reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ and propylene at room temperature. The spectrum was taken on a 500 MHz NMR spectrometer at 5 °C, and the resonances for the propyl group of *trans*-$Pt(Cl)(n\text{-}C_3H_7)(TPPTS)_2$ are shown.

tent with this scheme. When a solution of *trans*-$Pt(Cl)(C_2H_5)(TPPTS)_2$ was made basic by the addition of NaOH, deprotonation to $Pt(C_2H_4)(TPPTS)_2$ was not observed. Instead, *trans*-$Pt(OH)(C_2H_5)(TPPTS)_2$ was initially formed, which slowly isomerized into the thermodynamically favored cis isomer (NMR characterization is shown in Table 1). Similar behavior was seen for *trans*-$Pt(OH)(CH_3)(TPPTS)_2$.[10] $Pt(TPPTS)_3$ (5%) was formed as well, which is attributed to elimination of ethylene to form $Pt(H)(OH)(TPPTS)_2$. On the basis of our work, this species would be very unstable in solution, thus being converted into the stable Pt^0 complex in the basic solution.

Reactions with Propylene and 1-Hexene. Reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with propylene in water at room temperature produced *trans*-$Pt(Cl)(H)(TPPTS)_2$, $Pt(H)(TPPTS)_3^+$ (~30% combined), *trans*-$Pt(Cl)(n\text{-}C_3H_7)(TPPTS)_2$ (30%), and *trans*-$Pt(H_2O)(n\text{-}C_3H_7)(TPPTS)_2^+$ (14%). The remainder is starting complex. The ^{31}P NMR characterizations of the two propyl species are shown in Table 1. Shown in Figure 4 is the alkyl region of the ^1H NMR spectrum taken at 5 °C. The decreased temperature helped to resolve the H_α and H_β resonances, which overlap at room temperature. To assign the protons to the correct carbons on the propyl chain, we obtained a 1D ^1H TOCSY NMR spectrum of this region. In this experiment, a proton resonance is selectively irradiated and the magnetization is relayed along the carbon chain as a function of mixing time. Thus, by varying the mixing time we can determine which protons and, therefore, which carbons are adjacent to each other: i.e., at shorter mixing times protons close to the irradiated proton appear, while at longer mixing times protons further away begin to appear in the spectrum. Shown in Figure 5 is the result of selective irradiation of the resonance at δ −0.50 (t) ppm with varying mixing times at 5 °C. We chose this resonance because we believe it to be the terminal methyl group. The protons on this group would be split into a triplet due to the two neighboring protons on the adjacent methylene. Coupling due to the two ^{31}P and ^{195}Pt nuclei would be negligible, due to the distance of the bonds in the molecule. As can be seen in Figure 5, the resonance at δ 0.41 ppm was the first to appear at a mixing time of ~10 ms. Since this signal appears at such a short mixing time, these protons have to be adjacent to those being selectively irradiated. As the time was progressively increased to 70 ms, a second resonance appeared at δ 0.28 ppm. Since this signal appeared at longer mixing times, these protons correspond to those further on the propyl chain. On the basis of this evidence, we assigned the protons as shown in Figure 4. In addition to this NMR experiment, a 2D ^1H COSY spectrum was taken of this sample at room temperature. The results clearly showed coupling of protons H_γ and H_β. The coupling between H_β and H_α was difficult to determine, due to noise in the spectrum. Selective decoupling of H_β resulted in collapsing of the triplet at δ −0.50 ppm (H_γ) to a singlet. It was difficult to determine the effect of the decoupling on the resonance at δ 0.28 ppm (H_α), since this resonance is also split by the ^{195}Pt and ^{31}P nuclei. Both the ^{31}P and ^1H NMR characterizations for *trans*-$Pt(Cl)(n\text{-}C_3H_7)(TPPTS)_2$ are given in Table 1. We were unable to locate the NMR characterization of the PPh_3 analogue of this species in the literature. Romeo et al. reported the ^{31}P characterization of *trans*-$Pt(Cl)(n\text{-}C_3H_7)(PEt_3)_2$ at δ 35.6 ppm (s, $^1J_{Pt-P} = 2959$ Hz).[35] Clark and Kurosawa reported the ^1H NMR characterization of the propyl protons of *trans*-$[Pt(n\text{-}C_3H_7)(PPh_2Me)_2C)]PF_6$ ($C{=}\overline{COCH_2CH_2C}H_2$) at δ 0.82 (complex, H_α and H_β) and 0.54 ppm (t, H_γ).[36]

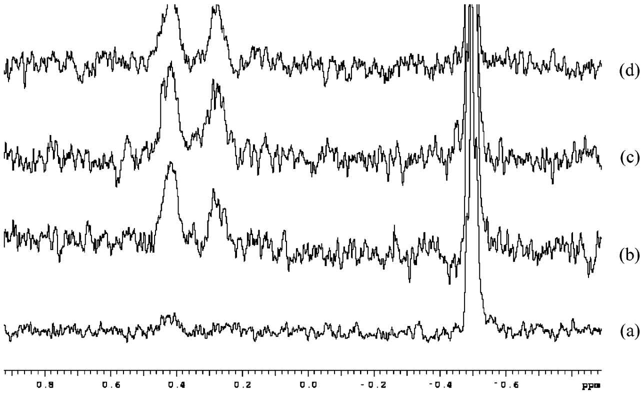


Figure 5. Array of ^1H NMR spectra, recorded on a 500 MHz NMR spectrometer at 5 °C, showing the effect of varying the mixing time in the 1D ^1H TOCSY NMR experiment: (a) 10 ms; (b) 30 ms; (c) 50 ms; (d) 70 ms.

It is known that insertion of alkenes into M−H bonds leads to various isomeric mixtures of the resulting alkyl species.[37] Thus, in our case, an equilibrium should exist between *trans*-$Pt(Cl)(n\text{-}C_3H_7)(TPPTS)_2$ and the isopropyl derivative. Studies conducted by Reger et al. on $[R_2NCS_2]Pt(PR'_3)(alkyl)$ (R = Me, Et; R′ = Et, Ph; alkyl = *n*-propyl, isopropyl) at 120 °C showed a ratio of 9:1.[37] Thus, the primary isomer is thermodynamically more stable than the secondary isomer. In our system, we could not identify any resonance that could be attributed to formation of an isopropyl complex.

Along with the formation of *trans*-$Pt(Cl)(n\text{-}C_3H_7)(TPPTS)_2$, we saw conversion of propylene to acetone. The amount of acetone was determined in a manner analogous to that for acetaldehyde in the case of ethylene. On the basis of these results, a mechanism

---

(35) Alibrandi, G.; Cusumano, M.; Minniti, D.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 342.

(36) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1972**, *11*, 1275.

(37) Reger, D. L.; Garza, D. G.; Baxter, J. C. *Organometallics* **1990**, *9*, 873.

similar to that described in reaction 7 occurred. The amount of acetone is stoichiometric with the Pt−H species formed. The pH change for this reaction is similar to that of the ethylene (initial pH ∼3, final pH ∼2). Addition of HBF_4 to the beginning solution showed inhibition of the reaction. Propanal can also be formed from propylene if anti-Markovnikov addition occurs. In the $PdCl_4^{2-}$-catalyzed Wacker oxidation of propylene, propanal is often seen as a product, in addition to acetone.[38] Propanal would result from anti-Markovnikov addition of a water or hydroxide molecule to the bound propylene. Results obtained by Henry showed the product yields of acetone and propanal to be 80−95% and 10−20%.[38] As can be seen from our results, in which acetone was formed exclusively, and those of Henry, the Markovnikov addition predominates; however, this is not always the case. In the oxidation of styrene, ∼75% was converted to phenylacetaldehyde.[39]

There are some marked differences between the ethylene and propylene reactions. When the reaction mixture is heated, less conversion of propylene to acetone was seen and numerous unidentified species were present in the ^{31}P NMR spectrum. Also, under basic conditions (pH ∼13) at room temperature, the only species present in the ^{31}P NMR was OTPPTS. No coordination of the propylene to the metal center was noted. This could be due to rapid dissociation of the propylene from the metal center. In addition, the β-hydride elimination is much more rapid for the propyl complex; characterization of the propyl complex requires a propene atmosphere.

A mechanism similar to reaction 7 appears to occur in the reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with 1-hexene. Reactions done at 25 °C revealed the formation of *trans*-$Pt(Cl)(H)(TPPTS)_2$ (6%); the starting material was largely unreacted after 24 h. GC/MS of the organic phase revealed the presence of 2-hexanone exclusively. The pH was relatively unchanged because only a small percentage of the starting material reacted. On the basis of the mechanism outlined in reaction 7, the amount of 2-hexanone should be stoichiometric with the formation of *trans*-$Pt(Cl)(H)(TPPTS)_2$. The limited reactivity of the 1-hexene was attributed to the poor water solubility of this substrate. Therefore, we added methanol as a cosolvent to the mixture at 25 °C, and 75% of the starting material was converted into *trans*-$Pt(Cl)(H)(TPPTS)_2$ after 24 h. The hydride resonance was clearly present in the ^1H NMR spectrum at δ −16.6 (t). Reaction of *cis*-$Pt(Cl)_2(TPPTS)_2$ with 1-hexene at 60 °C in H_2O alone resulted in ∼50% of the starting material being converted into a mixture of bis- and tris-phosphine hydrides. Reaction at 60 °C in H_2O/MeOH resulted in exclusive formation of *trans*-$Pt(Cl)(H)(TPPTS)_2$ and a stoichiometric amount of 2-hexanone. $Pt(H)(TPPTS)_3^+$ was not present; thus, the bis-phosphine species is very stable in this mixed-solvent system. Reactions in dried CH_3OH showed no oxidation of 1-hexene; the *cis*-$Pt(Cl)_2(TPPTS)_2$ was insoluble. Again, up to 60 °C, the reaction in H_2O and H_2O/MeOH follows the mechanism outlined in reaction 7. The amounts of 2-hexanone were stoichiometric with the hydride complex. In a related system, Sheldon et al. observed 43% conversion of 1-hexene to 2-hexanone when reacting $(N{-}N)Pd(OAc)_2$ (N−N = sulfonated bathrophenanthroline) in water.[40] The addition of 50 equiv of $[NEt_3(PhCH_2)]Cl$ as a phase transfer reagent to the solution of *cis*-$Pt(Cl)_2(TPPTS)_2$ resulted in less reactivity with 1-hexene, probably because this phase transfer reagent contains Cl^- and increased concentrations of Cl^- in solution deterred the reaction. As shown in reaction 7, Cl^- dissociation from the metal center is a prerequisite for reactivity.

Summary. In conclusion, we have shown that reactions of ethylene, propylene, and 1-hexene proceed through a Wacker-type mechanism to afford acetaldehyde, acetone, and 2-hexanone, respectively. These results help support the mechanism of Wacker oxidation and the various aspects seen in the $PdCl_4^{2-}$-catalyzed reaction. We also showed that control over the pH is very important in determining the reactivity of the complex in solution. Under very acidic conditions, only traces of the three organic products were seen, and under basic conditions, coordination was observed only for C_2H_4. The catalytic conversion of C_2H_4 to CH_3CHO by *cis*-$Pt(Cl)_2(TPPTS)_2$ at higher temperatures suggests a new mechanism and offers the possibility for catalytic formation of CH_3CHO without a cocatalyst, with water as the solvent and reactant.

Experimental Section

Materials. Ethylene and propylene were purchased from Matheson and used as received. D_2O, d_6-DMSO, d_4-ethylene, d_6-benzene, methanol, and 1-hexene were purchased from Aldrich Chemical Co. 1-Hexene was fractionally distilled prior to use, and dry methanol was produced by fractional distillation, followed by refluxing over CaH_2 overnight and distilling under N_2. Water was triply distilled and purged with N_2 prior to use. *cis*-$Pt(Cl)_2(TPPTS)_2$, $Pt(Cl)(TPPTS)_3^+$, and *cis*-$[Pt(H_2O)_2(TPPTS)_2]^{2+}$ were previously reported and characterized.[33]

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 or 500 MHz spectrometer at room temperature, unless otherwise stated. ^{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 is set at −1627 ppm.[41] A coaxial inner cell filled with d_6-DMSO was used for the measurement of NMR spectra in H_2O. 2D ^1H COSY and 1D ^1H TOCSY were both recorded on a 500 MHz spectrometer at the specified temperature. pH measurements were performed using a Fischer Scientific Accumet basic pH meter by Denver Instruments Inc. with a semimicro glass pH electrode and a silver/silver chloride reference electrode. The pH electrode was calibrated at pH 4, 7, and 10 using buffers. All GC/MS analyses were done on a HP 5890 Series II gas chromatograph with an HP 5972 series mass selective detector, containing a Supelco SPB-5 fused silica capillary column: 30 m × 0.25 mm × 0.25 μm.

General Procedure for Pt-Catalyzed Reactions Involving High Pressures (>1 atm) of Ethylene and Pro-

---

[38] Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81.
[39] Reference 7e, pp 46−47.
[40] ten Brink, G.-J.; Arends, I. W. C. E.; Papadogianakis, G.; Sheldon, R. A. *Chem. Commun.* **1998**, 2359.
[41] Hollis, S. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3494.

pylene. These reactions were performed in a Parr Model No. 4592 micro high temperature and pressure reactor, equipped with a Model No. 4842 display unit. The reactor contains a 50 mL stainless steel bomb, equipped with a stainless steel automatic stirrer. A glass reaction vessel was used to contain the solution inside the bomb. A heating mantle was used to heat the bomb if required. In a typical experiment, approximately 55 mg of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ was dissolved in exactly 3 mL of the given solvent (H_2O or D_2O). Three drops of 10% NaOH were added to the solution for reactions run under basic conditions. The reactor was purged with the appropriate gas three times and then left at the desired pressure (31 atm for ethylene and 9.0 atm for propylene). Upon completion of the reaction (usually 18 h unless stated otherwise), the bomb was cooled to room temperature (if heated) before being depressurized. A 0.5 mL aliquot of the resulting solution was removed and placed into an NMR tube. A coaxial inner cell containing d_6-DMSO was used to take NMR spectra of solutions in nondeuterated solvents.

Procedure for the Pt-Catalyzed Reaction Utilizing C_2D_4. These reactions were performed in a 100 mL pressure tube containing a small stir bar. In a typical experiment, approximately 20 mg of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ was dissolved in exactly 1 mL of triply distilled water and placed into the pressure tube. The tube was subjected to three freeze−pump−thaw cycles before being left under vacuum. The tube was then pressurized to −1 atm with C_2D_4 (g). Upon completion of the reaction (18 h), a 0.5 mL aliquot of the resulting solution was removed and placed into an NMR tube. A coaxial inner cell containing d_6-DMSO was used for the measurement of NMR spectra.

General Procedure for Pt-Catalyzed Reactions involving 1-Hexene. These reactions were performed in a 20 mL Carius tube modified with a 14/20 joint. A micro stir bar was placed into these vessels to stir the reactants, unless otherwise noted. Once the reactants had been added, the contents were subjected to three freeze−pump−thaw cycles and then flame sealed under vacuum. In a typical experiment, approximately 17 mg of *cis*-Pt(Cl)$_2$(TPPTS)$_2$ was dissolved in exactly 1.0 mL of the appropriate solvent (in H_2O/MeOH, 0.5 mL of each was used). To this solution was added 1.0 mL of distilled 1-hexene. Upon completion of the reaction, the tubes were scored with a metal file and opened to the atmosphere. The resulting organic phases were collected and placed into GC autosampler vials and analyzed by GC/MS. A 0.5 mL aliquot of the resulting aqueous phase was placed into an NMR tube for analysis. A coaxial inner cell containing d_6-DMSO was used for the measurement of NMR spectra of solutions in nondeuterated solvents.

Acknowledgment. Support of this research by the Department of Energy (Grant No. ER 13775) is gratefully acknowledged. Dr. Dinesh Sukumaran was invaluable in designing and interpreting the TOCSY NMR experiments. D.S.H. is grateful for a Silbert Fellowship and a DOE Award for the Nobel Laureates Meeting in Lindau, Germany, 2002. We are grateful to the Gardella research group, especially Rich Nowak, for assistance with the XPS data.

OM030500B