4116 *Organometallics* **1996,** *15,* 4116−4118

Synthesis, Characterization, and Reactivity of New Platinum(II) Alkyl Alkene Complexes

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Received June 18, 1996[⊗]

*Summary: A new Pt(II) ethyl ethene complex, $[Pt(\mu\text{-}Cl)(CH_2CH_3)(C_2H_4)]_2$, (**1**), was isolated from the reaction of ethene with K_2PtCl_4 in water, and the structure was confirmed by X-ray crystallography. The results of oxidation experiments involving **1** indicate that $Pt^{II}-C_2H_5$ and $Pt^{II}-(CH_2{=}CH_2)$ species are viable intermediates in the conversion of ethane to ethanol and ethane-1,2-diol by the Shilov system.*

The selective activation and functionalization of C−H bonds in alkanes is one of the most challenging problems in chemistry. Shilov and co-workers were the first to demonstrate metal-mediated alkane functionalizations in water, showing that simple Pt(II) complexes, such as $PtCl_4^{2-}$, activate and oxidize the C−H bonds of alkanes.[1] We,[2] as well as Bercaw and Labinger,[3] have shown that this system can functionalize a wide variety of substrates with unusual selectivity. Although the system has been studied in some detail, the mechanism of these reactions remains unclear. The prevailing hypothesis is that a Pt(II)−alkyl species is initially formed by an electrophilic C−H cleavage step. This Pt(II)−alkyl species is subsequently converted (oxidized) to form the products. In the specific case of ethane, the observed organic products are ethanol and ethane-1,2-diol.[2a,c,d] Through labelling experiments, we have shown that ethanol is *not* an intermediate for the latter compound;[2a,c] rather, ethane-1,2-diol is formed from Zeise's salt, $[Pt(Cl)_3(C_2H_4)]^-$ (or its dimer).[2a,3a] This Pt(II) species is observed as an intermediate in the reaction of $PtCl_4^{2-}$ with ethane[2d] and is presumably formed from a Pt(II)−C_2H_5 intermediate through a β-hydrogen-abstraction step. To better understand the mechanism of this series of reactions, Pt(II)−alkyl and Pt(II)−alkene complexes similar to the ones likely to be involved in the Shilov system, i.e. complexes lacking strong donor ligands, must be studied. Only one such complex has ever been isolated and characterized, $[Pt(\mu\text{-}Cl)(CH_3)(C_2H_4)]_2$, synthesized by Puddephatt through the alkylation of Zeise's dimer, $[Pt(\mu\text{-}Cl)(Cl)(C_2H_4)]_2$.[4] The reaction of this complex with oxidants has not been reported. Herein, we report (a) the synthesis of a class of $Pt^{II}(C_2H_5)$(alkene) complexes through the reaction of $PtCl_4^{2-}$ with ethene in water, (b) the structural characterization of the first such complex by X-ray crystallography, and (c) the reactivity and oxidation chemistry of such complexes.

The complex $[Pt(\mu\text{-}Cl)(C_2H_5)(C_2H_4)]_2$, (**1**) was prepared in the following manner. A 0.04 g amount of K_2PtCl_4 was dissolved in 2 mL of water in a glass liner with a magnetic stirring bar. The liner was then put in a bomb which was then charged with 800 psi of ethene, and the mixture was stirred at ambient temperature for 5 days. Following the release of pressure, the glass liner contained a pale yellow solution and a white solid. The latter was extracted with $CDCl_3$ and yielded **1** in 70% yield after drying and removal of solvent. The water layer was acidic (pH ∼1) and contained Zeise's salt, $[Pt(Cl)_3(C_2H_4)]^-$, and acetaldehyde.

Complex **1** was characterized by NMR spectroscopy and X-ray crystallography. The ambient-temperature ^1H NMR spectrum in $CDCl_3$ showed a pseudotriplet (singlet flanked by doublet, the latter due to coupling with ^{195}Pt) at 3.70 ppm ($^2J_{Pt-H} = 81.0$ Hz, 4H), a pseudotriplet of quartets at 1.20 ppm ($^2J_{Pt-H} = 80.2$ Hz, $^3J_{H-H} = 7.5$ Hz, 2H), and a pseudotriplet of triplets at 0.69 ppm ($^3J_{Pt-H} = 37.0$ Hz, $^3J_{H-H} = 7.4$ Hz, 3H). At 213 K the coordinated ethene resonances split into two pseudotriplets of doublets at 3.86 ppm ($^3J_{Pt-H} = 87.3$, $^3J_{H-H} = 14.1$ Hz, 2H) and 3.42 ppm ($^3J_{Pt-H} = 73.7$, $^3J_{H-H} = 14.1$ Hz). These doublets have an internal coupling pattern similar to that of para-substituted benzenes and indicated that the two hydrogens on each ethene carbon become inequivalent at low temperature. The ambient-temperature $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$ consisted of a pseudotriplet at 63 ppm ($^1J_{Pt-C} = 259.7$ Hz), a pseudotriplet at 16.1 ppm ($^2J_{Pt-C} = 34.2$ Hz), and a third pseudotriplet at 9.0 ppm ($^1J_{Pt-C} = 657.3$ Hz). ^{195}Pt NMR showed a broad singlet at −1943 ppm.

The structure of **1** was confirmed by single-crystal X-ray crystallography (Figure 1).[5] The overall structure is unexceptional, with a planar geometry around each Pt atom and the C−C axes of the coordinated ethenes orthogonal to that plane. The C−C distances in the ethenes are longer than that in Zeise's salt, $[Pt(Cl)_3(C_2H_4)]^-$ (1.41 versus 1.37 Å), and the C−C distances

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

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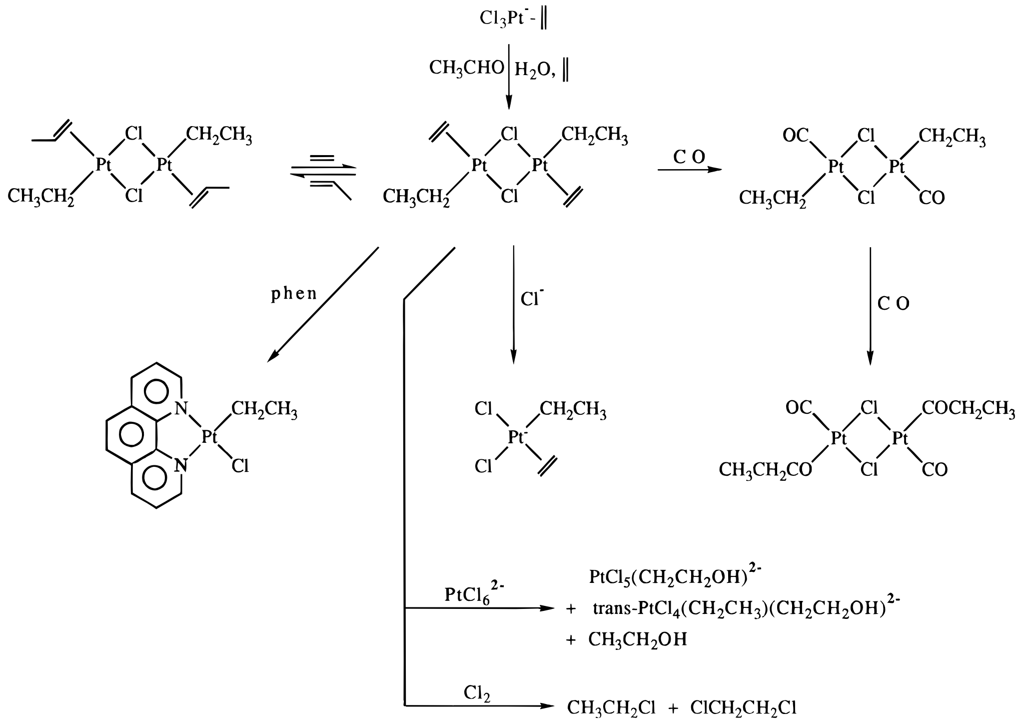
(5) Crystal data for $C_8H_{18}Cl_2Pt_2$: monoclinic, $P2_1/c$, $a = 10.424(5)$ Å, $b = 8.357(3)$ Å, $c = 7.434(3)$ Å, $\beta = 109.77(3)°$, $V = 609.5(5)$ Å^3, $Z = 2$, $T = 265$ K, μ(Mo Kα) = 233 cm^{-1}, $D_{calcd} = 3.135$ g cm^{-3}, $R(F) = 6.29\%$ for 1767 observed independent reflections ($4° \leq 2\theta \leq 60°$). Semiempirical absorption corrections were applied. All non-hydrogen atoms were treated as idealized contributions.

S0276-7333(96)00495-5 CCC: $12.00

Scheme 1



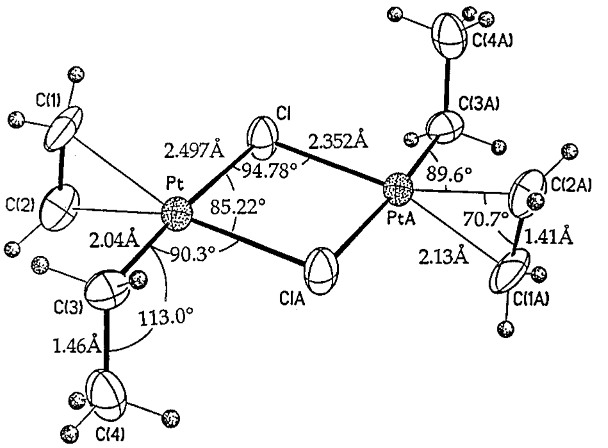
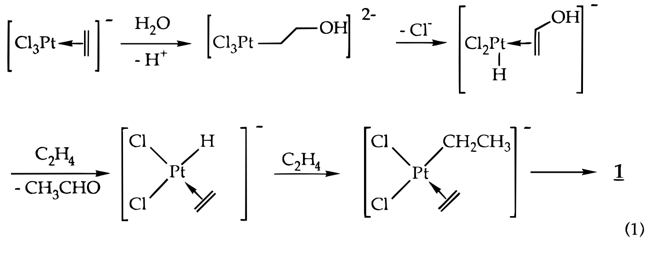


Figure 1. Structure of $[Pt(\mu\text{-}Cl)(CH_2CH_3)(C_2H_4)]_2$, as determined by X-ray diffraction.

in the ethyl groups are significantly shorter than that expected for a sp^3–sp^3 bond (1.46 versus 1.54 Å).

The formation of **1** presumably occurred through the sequence of steps given in eq 1. $[Pt(Cl)_3(C_2H_4)]^-$ was



(1)

initially formed in the reaction of $PtCl_4^{2-}$ with ethene. Zeise's salt could subsequently react to form vinyl alcohol and a platinum hydride by nucleophilic attack of water followed by a β-hydride elimination. The formation of acetaldehyde as a side product was also observed. It is not known at what point dimerization occurred; $[Pt(Cl)_3(C_2H_4)]^-$ is known to dimerize under acidic conditions.[4]

The chemistry of **1** is summarized in Scheme 1. The dimer could be split apart by stirring **1** in NaCl-saturated D_2O for 2 days, resulting in the formation of $Na[Pt(Cl)_2(CH_2CH_3)(C_2H_4)]$. The ^1H NMR spectrum in D_2O at ambient temperature of this species consisted of a pseudotriplet at 3.99 ppm ($^3J_{Pt-H} = 77.0$ Hz, 4H), a pseudotriplet of quartets at 1.44 ppm ($^2J_{Pt-H} = 77.8$, $^3J_{H-H} = 7.5$ Hz, 2H), and a pseudotriplet of triplets at 1.04 ppm ($^3J_{Pt-H} = 40.3$, $^3J_{H-H} = 7.4$ Hz, 3H). $Na[Pt(Cl)_2(CH_2CH_3)(C_2H_4)]$ was found to be less stable than the dimer **1** and started to decompose after 24 h.

The addition of 1,10-phenanthroline to a $CDCl_3$ solution of **1** also split apart the dimer to form ethene and (1,10-phenanthroline)$Pt(Cl)(CH_2CH_3)$. In the ^1H NMR spectrum, the former appeared as a singlet at 5.35 ppm. The ethyl group in the latter species appeared as a pseudotriplet of quartets at 2.21 ppm ($^2J_{Pt-H} = 85.2$, $^3J_{H-H} = 7.8$ Hz, 2H) and a pseudotriplet of triplets at 1.17 ppm ($^3J_{Pt-H} = 33.6$, $^3J_{H-H} = 7.7$ Hz, 3H). The protons next to the nitrogen on 1,10-phenanthroline also exhibited ^{195}Pt coupling, showing up as two pseudotriplets of a doublet of doublets at 9.51 ppm ($^3J_{Pt-H} = 62.1$, $^3J_{H-H} = 5.5$, $^4J_{H-H} = 1.1$ Hz, 1H), and 9.82 ppm ($^3J_{H-H} = 5.0$, $^4J_{H-H} = 1.4$ Hz, 1H, Pt coupling too indistinct to measure).

The coordinated ethene was replaced by propene when **1** in $CDCl_3$ was exposed to 150 psi of propene overnight. The ^1H NMR spectrum in CD_2Cl_2 at 213 K revealed the following resonances for the coordinated propene: a broad pseudotriplet of pentets of doublets at 4.07 ppm ($^3J_{Pt-H} = 84$ Hz, $^3J_{H-H} = 6.3$ Hz, $^3J_{H-H} =$ 2.2 Hz, 1H), two pseudotriplets of doublet of doublets at 3.55 ppm ($^3J_{Pt-H} = 72.4$ Hz, $^3J_{H-H} = 13.1$ Hz, $^1J_{H-H}$ $= 4.5$ Hz, 1H) and 3.37 ppm ($^3J_{Pt-H} = 83.0$ Hz, $^3J_{H-H} =$ 10.5 Hz, $^1J_{H-H} = 7.3$ Hz, 1H), and a pseudotriplet of doublets at 1.62 ppm ($^3J_{Pt-H} = 55.1$ Hz, $^3J_{H-H} = 5.9$

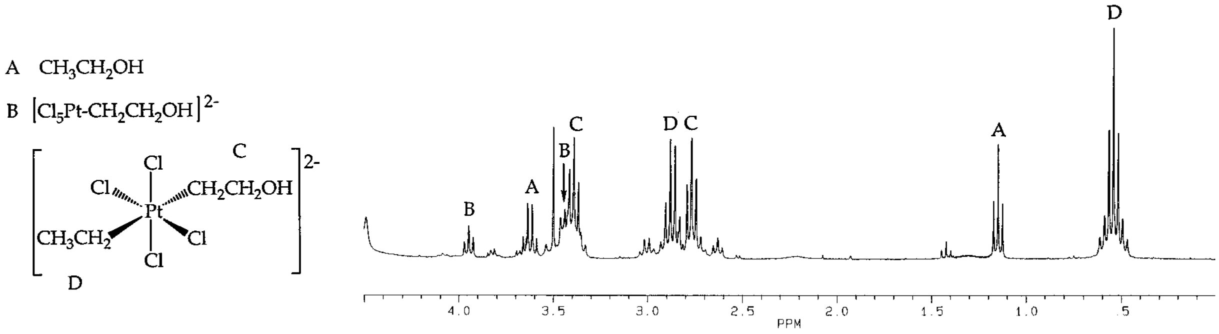


Figure 2. ^{1}H NMR spectrum obtained after $[Pt(\mu\text{-}Cl)(CH_2CH_3)(C_2H_4)]_2$ was allowed to react with Na_2PtCl_6 in D_2O at ambient temperature for 2 days.

Hz, 3H). Not unexpectedly, the propene complex reformed **1** upon reaction with ethene.

When **1** was allowed to react with 1 atm of CO for 10 min at ambient temperature, the coordinated ethene was replaced by CO to form $[Pt(\mu\text{-}Cl)(C_2H_5)(CO)]_2$. The ^{1}H NMR showed a pseudotriplet of quartets at 2.13 ppm (${}^2J_{Pt-H} = 84.9$ Hz, ${}^3J_{H-H} = 7.5$ Hz, 2H) and a pseudotriplet of triplets at 1.12 ppm (${}^3J_{Pt-H} = 68.0$ Hz, ${}^3J_{H-H} = 7.5$ Hz, 3H). When ^{13}CO was used, the ^{13}C NMR spectrum showed a pseudotriplet at 159 ppm (${}^1J_{Pt-C} = 2404$ Hz) due to coordinated carbon monoxide and resonances at 18.5 and 9.5 ppm for the ethyl group. Upon prolonged reaction with ^{13}CO (40 psi, overnight), the ^{1}H NMR spectrum showed a pentet at 2.80 ppm (${}^3J_{H-H} = 7.2$ Hz, 2H), and a quartet at 1.08 ppm (${}^3J_{H-H} = 7.2$ Hz, 3H). The ^{13}C NMR spectrum showed a pseudotriplet at 187.5 ppm (${}^1J_{Pt-C} = 766.7$ Hz), another pseudotriplet at 157.5 ppm (${}^1J_{Pt-C} = 2502$ Hz), a doublet at 48.5 (${}^1J_{C-C} = 35.4$ Hz), and a singlet at 9.5 ppm. These peaks correspond to $[Pt(\mu\text{-}Cl)({}^{13}C(O)C_2H_5)({}^{13}CO)]_2$. After it stood for a few days at ambient temperature, the complex reacted with trace water in solution to form propionic acid. Thus, the overall stepwise transformation serves as a good model for the Reppe reaction[6] (eq 2).

$$CH_2{=}CH_2 + CO + H_2O \rightarrow CH_3CH_2COOH \quad (2)$$

The facile insertion of carbon monoxide into the $Pt^{II}-C$ bond of **1** stands in sharp contrast to the reluctance of the $Pt^{IV}-C$ bond of $[Pt(Cl)_5R]^{2-}$ to undergo similar insertion. For example, when $[Pt(Cl)_5(CH_3)]^{2-}$ [2d,3a,7] was exposed to 1 atm of CO at ambient temperature, the only organometallic species observed was $[Pt(Cl)_4(CH_3)_2]^{2-}$, which exhibited a ^{1}H NMR pseudotriplet at 1.81 ppm (${}^2J_{Pt-H} = 78$ Hz). The formation of the new Pt(IV) species was confirmed by its conversion to $[Pt(glycine)(Cl)_2(CH_3)_2]^-$,[8] whose ^{1}H NMR spectrum (two pseudotriplets at 1.54 ppm (${}^2J_{Pt-H} = 76$ Hz) and 1.39 ppm (${}^2J_{Pt-H} = 68$ Hz)) was closely analogous to that of the previously reported $[Pt(glycine)Br(OH)(CH_3)_2]^-$.[9]

Finally, we have examined the oxidation of **1** by Cl_2 and $PtCl_6^{2-}$. When Cl_2 was added to a solution of **1** in $CDCl_3$, no clear platinum(IV) intermediates were seen, even when the reaction was run at −78 °C. The principal products were ethyl chloride and 1,2-dichloroethane.

Complex **1** was found to react with Na_2PtCl_6 in the presence of water at ambient temperature. The proton NMR showed several Pt(IV) species and ethanol (see Figure 2). One of the complexes was $[Pt(Cl)_5(CH_2CH_2OH)]^{2-}$ (a pseudotriplet of triplets at 3.95 ppm (${}^2J_{Pt-H} = 63.6$ Hz, ${}^3J_{H-H} = 7.1$ Hz, 2H) and a triplet at 3.44 ppm (${}^3J_{H-H} = 6.8$ Hz, 2H)), which can also be formed by the oxidation of Zeise's salt, $[Pt(Cl)_3(C_2H_4)]^-$,[2a,3a] and is known to be the key intermediate in the formation of ethane-1,2-diol from ethene and ethane in the Shilov system.[2a,c,d] Additionally, there was a $Pt^{IV}-C_2H_5$ (a pseudotriplet of quartets at 2.87 ppm (${}^2J_{Pt-H} = 81.5$ Hz, ${}^3J_{H-H} =7.5$ Hz, 2H) and a pseudotriplet of triplets at 0.54 ppm (${}^3J_{Pt-H} = 28.6$ Hz, ${}^3J_{H-H} = 7.4$ Hz, 3H)) and a second $Pt^{IV}-CH_2CH_2OH$ species (a pseudotriplet of triplets at 2.77 ppm (${}^2J_{Pt-H} = 82.4$ Hz, ${}^3J_{H-H} = 7.1$ Hz, 2H) and a triplet at 3.39 ppm (${}^3J_{H-H} = 7.2$ Hz, 2H)). The two organic fragments may be trans to each other on the same Pt atom; the integrals corresponded within error, but there was no NOE correspondence.

In conclusion, we have shown that Pt(II)−alkyl complexes lacking strong donor ligands are stable and can be structurally characterized. Additionally, the results of the oxidation experiment involving Na_2PtCl_6, together with previous reports,[2a,c,d,3a] clearly indicate that $Pt^{II}-C_2H_5$ and $Pt^{II}-(CH_2{=}CH_2)$ species are viable intermediates in the conversion of ethane to ethanol and ethane-1,2-diol by the Shilov system.

Acknowledgment. This research was funded by the National Science Foundation.

Supporting Information Available: For **1**, tables of crystal data and structure refinement, atomic coordinates, bond lenghts and bond angles, anisotropic displacement coefficients, and H-atom coordinates (5 pages). Ordering information is given on any current masthead page.

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