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PLATINUM(II) CATALYZED ALKOXIDE EXCHANGE AND ISOMERIZATION OF VINYL ETHERS

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Summary

Alkoxide exchange of vinyl ethers (RCH=CHOR') with alcohols is catalyzed by both $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ (I) and $t\text{-}[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5\text{N})]$ (II). The catalytic *cis*-*trans* isomerization of substituted vinyl ethers by II has been achieved by conducting the reaction in acetonitrile solvent.

Introduction

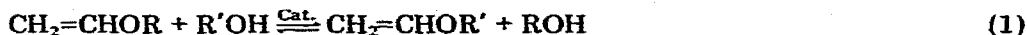
Although hundreds of alkeneplatinum(II) complexes have been prepared and characterized, no olefin isomerization either during the coordination of the alkene, or during its displacement, has ever been observed. However, the closely related vinyl ethers in $[\text{PtCl}_2(\text{RCH}=\text{CHOR}')]_2$ have been reported to undergo thermal *cis*-*trans* isomerization around the double bond when heated either neat or in toluene solution [1]*. Similar isomerization has also been shown to occur in the course of the displacement of the vinyl ether by pyridine [1]. The thermal isomerization has been ascribed to some (unspecified) interaction between the ether oxygen and the platinum(II) atom while the isomerization with pyridine has been ascribed [1] to $\pi \rightarrow \sigma$ rearrangement with the formation of a zwitterion intermediate of the type first shown to occur with alkenes [2]. However, such isomerization is possible only if the pyridine attack and departure are non-stereospecific. Recent work [3] on pyridine (Py) promoted $\pi \rightarrow \sigma$ interconversion with $t\text{-}[\text{PtCl}_2(\text{cis}\text{-C}_2\text{H}_2\text{D}_2)(\text{Py})]$ shows this is not the case with ethylene (and probably other alkenes).

The present study was undertaken in order to develop a catalytic system for vinyl ether isomerization and to resolve the uncertainty with respect to the reported stoichiometric isomerizations described above. We wish to report here success in realizing the first objective and partial success with the second.

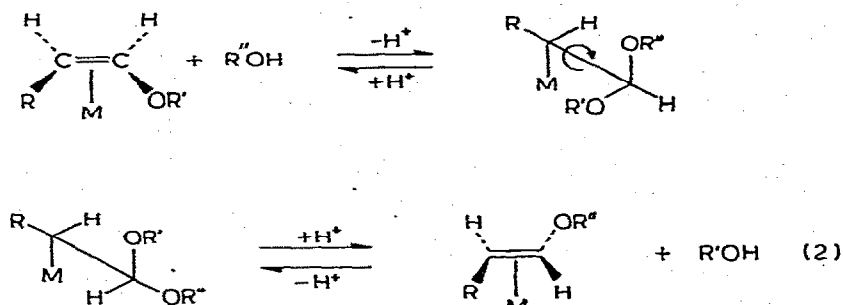
* We have performed an X-ray crystal analysis of the vinyl ether complex $\text{Et}_4\text{N}^+[\text{PtCl}_3(\text{CH}_2=\text{CHOEt})]^-$ and found that the O atom is farther removed from the Pt than the HCH methylenide grouping [1b].

Results and discussion

The starting point for our exploration of the mechanism of vinyl ether isomerization was the known alkoxide exchange reaction. Coordinated vinyl ethers have been shown to undergo a catalytic exchange of OR groups in the presence of metal complexes such as mercuric acetate and $[\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ (eq. 1).



This exchange has been demonstrated to involve a stereospecific addition-elimination [4] and consequently *cis* \rightleftharpoons *trans* isomerization may occur during the exchange of substituted vinyl ethers (eq. 2).



If, in our experiments, the required traces of alcohol were present, then our observed isomerization could be ascribed to catalytic exchange accompanied by isomerization. Free alcohol could conceivably arise via metal (or acid) catalyzed hydrolysis of vinyl ether by adventitious water. Accordingly a study was undertaken of the platinum(II) catalyzed alkoxide exchange since such exchange with platinum(II) has not heretofore been reported.

Alkoxide exchange using either $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ (I) or $t\text{-}[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{Py})]$ (II)

Both complexes I and II have been found to be effective catalysts for the alkoxide exchange of simple (mono-substituted ethylenes) vinyl ethers (Table 1).

TABLE I
VINYL ETHER (VE) EXCHANGE REACTIONS ($\sim 25^\circ\text{C}$)

Catalyst	RCH=CHOR' R	R'	VE/Cat.	ROH R	ROH/Cat.	Time (h) ^a
I ^b	H	Et	160	n-Bu	160	3
I	H	n-Bu	170	Et	170	3
II ^c	H	Et	63	n-Bu	63	6
II	H	n-Bu	61	Et	61	6
II + Py ^d	Me	Et ^e	35	Me	33	7
II + Py ^d	Me	Et ^e	80	Et	79	7
II	Me	Et ^e	33	Et	29	f

^aTo reach equilibrium. ^bI is $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$. ^cII is $t\text{-}[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{Py})]$. ^d8/1 moles Py/Pt. ^e*cis*-Isomer. ^fNot equilibrated after 3 weeks.

The vinyl ether displaces ethylene from its complexes very rapidly to give the corresponding π -vinyl ether complexes which then undergo exchange with $R'OH$ in accordance with eq. 1. With olefin/catalyst ratios of $\sim 100/1$, alkoxide exchange reaches equilibrium in 3–6 h at room temperature. Acetal formation accompanies the exchange reaction but at a significantly slower rate. Using substituted vinyl ethers, $RCH=CHOR'$, the dimeric catalyst I is still effective but with catalyst II, almost two weeks at room temperature are required to equilibrate a 30/1 olefin/Pt mixture. Addition of pyridine enormously enhances the catalysis by II; thus with $CH_3CH=CHOEt$ (ethyl propenyl ether) the rate approaches that of the corresponding reaction with unsubstituted vinyl ethers.

In an attempt to more clearly define the mechanism of the alkoxide exchange, $EtOD$ was used as the exchange agent in a solution containing $CH_2=CHOC_4H_9$, with II as catalyst. The exchange product, $CH_2=CHOEt$, was isolated and 1H NMR showed no D incorporation. In a second experiment the stereospecificity was studied by equilibrating *cis*- $CH_3CH=CHOEt$ with methanol in the presence of II. In the early stages of this reaction the *trans*-methyl propenyl ether predominates as expected for *trans*-addition—*trans*-elimination. These results are consistent with the mechanism of eq. 2 and indicate that, were small amounts of alcohol present in our vinyl ether isomerization system, the isomerization could conceivably be due to its presence. Accordingly, the displacement (accompanied by isomerization) when $t-[PtCl_2(cis-CH_3CH=CHOEt)(Py)]$ is treated with excess Py was repeated but under rigorous anhydrous conditions. Isomerization still occurred at about the same rate and it is therefore unlikely that the observed isomerization could be due to alkoxide exchange.

In order to extend the generality of the alkoxide type exchange process with a platinum(II) catalyst, the exchange of the RO group of the coordinated vinyl ether by R_2N derived from R_2NH was also investigated. Thus treatment of complexed ethyl vinyl ether with diethylamine resulted in the replacement of the ethoxy group by the diethylamino group in a reaction sequence analogous to eq. 2.

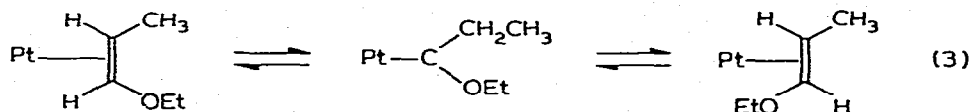
Catalytic isomerization

Although the isomerization of complexed vinyl ethers can be achieved during their displacement (stoichiometric isomerization), there are no reports of catalytic isomerization. Our early attempts to promote the catalytic isomerization with pyridine were unsuccessful because the platinum(II) is removed from solution by precipitation of the very insoluble $t-[PtCl_2(Py)_2]$. In an attempt to minimize the rate of formation of the insoluble platinum salts, hindered pyridines were employed but neither 2,6-di-*t*-butylpyridine nor 2,4,6-trimethylpyridine were effective. Some catalysis was eventually achieved (1.6 turnover efficiency) by careful control of excess pyridine. However, the use of acetonitrile finally provided a catalytic system. On treatment of 80 parts of *cis*- $CH_3CH=CHOEt$ with 1 part of II in acetonitrile solution, thermodynamic equilibrium of *cis* and *trans* isomers was achieved in 20 h at 70°C. *cis*- $PhCH=CHOCH_3$ was likewise isomerized with II at 60°C and equilibrium with the *trans* isomer was again achieved in 20 h.

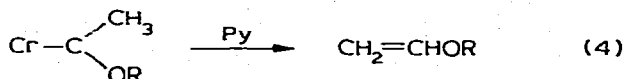
Comments on mechanism

Having ruled out the possibility of the *cis*—*trans* isomerization of vinyl

ethers proceeding through alkoxide exchange, other potential mechanisms were considered. One possible mechanism involves the intermediacy of a carbene species (eq. 3).

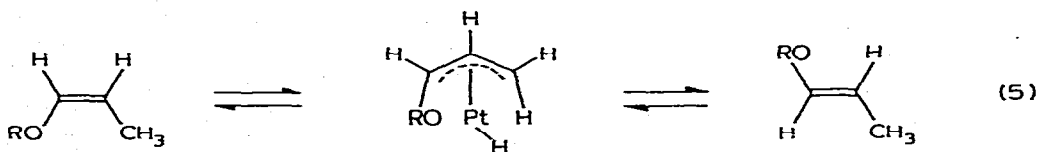


It has been shown [5] that displacement of an alkoxy carbene from its complex with chromium gives a vinyl ether (eq. 4). If a carbene complex were an



intermediate as shown in eq. 3, then the two hydrogens at the double bond become equivalent. In order to determine whether in fact this occurs in our system, $t\text{-[PtCl}_2(\text{cis-CH}_3\text{CD=CHOEt})(\text{Py})]$ was treated with pyridine and the liberated mixture of *cis*- and *trans*-vinyl ethers was isolated (GLC) and examined by ^1H NMR. No change in either the position or content of the ^2H was observed.

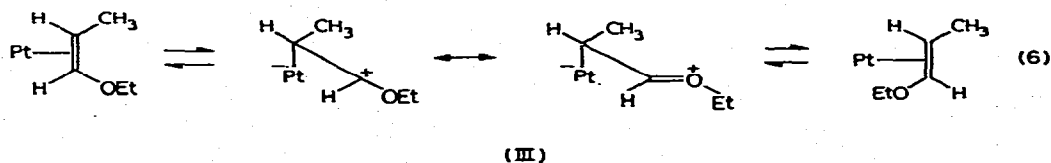
In an alternative mechanism, one may postulate abstraction of allylic hydrogen and the formation of a π -allyl intermediate to explain vinyl ether isomerization (eq. 5). Were this the only route to isomerization, then the vinyl ether, PhCH=



CHOCH_3 , which has no allylic hydrogen, should fail to undergo isomerization. However, this ether very readily undergoes *cis* \rightleftharpoons *trans* isomerization.

An additional alternate route to isomerization consists of the possibility of intermolecular formation of a small amount of the hydrido species, Pt-H , during the course of the reaction. Cationic platinum hydrides have been shown [6] to rearrange allyl ethers to propenyl ethers. Accordingly, $t\text{-[PtCl}_2(\text{CH}_2 = \text{CHCH}_2\text{OEt})(\text{Py})]$ was prepared and treated with pyridine under conditions which isomerize vinyl ethers. However, no vinyl ethers could be detected in the mixture.

The most probable pathway for the nucleophilic assisted vinyl ether isomerization consists of generating a trigonal carbon species by a $\pi \rightleftharpoons \sigma$ conversion of coordinated vinyl ether, e.g. eq. 6.



The interconversion may occur thermally via a unimolecular process or it may

occur by nucleophilic attack. There are two sites at which such attack may occur; either directly on the metal to form a 5-coordinated species, the well-known intermediate for ligand—ligand exchange in square planar platinum(II) complexes, or at the olefinic site. Pyridine—pyridine exchange occurs very rapidly [3] and pyridine—olefin exchange much more slowly. It is not known for certain whether one of the already-coordinated pyridines in the 5-coordinated intermediate attacks the vinyl ether or whether the attack is external. In either case, such attack could lead to isomerization by formation of III, loosely coordinated to pyridine or acetonitrile. The relative stability of III, due to delocalization of the positive charge, may lead to a sufficiently long life time for III to allow for rotation around the carbon—carbon bond essential for isomerization. The successful catalytic isomerization with acetonitrile undoubtedly resides in the fact that acetonitrile keeps the platinum complex in solution but it is also possible that it complexes less tightly with III than does pyridine.

Experimental

Reagent grade solvents were routinely dried over molecular sieves. For special anhydrous conditions, the solvents toluene, benzene, and THF were distilled from sodium; acetonitrile from P_2O_5 ; and pyridine from KOH. In order to assure the absence of any acid in acetonitrile, this solvent was stored over solid K_2CO_3 before use in the catalytic experiment described below. *cis*- $C_6H_5CH=CHOEt$ [7], methyl propenyl ether [8], *t*-[PtCl₂(C₂H₄)(Py)] [9], *t*-[PtCl₂(C₂H₄)-(2,4,6-Me₃Py)] [9], [PtCl₂(C₂H₄)₂] [10] were prepared according to literature procedures. Ethyl vinyl ether, butyl vinyl ether, and ethyl propenyl ether were distilled prior to use. The *cis* and *trans* isomers of ethyl propenyl ether were separated by distillation on a Podbielniak concentric tube column. GLC analyses of vinyl ethers were conducted on either a SE-30 or Carbowax 20M column. Proton NMR spectra were recorded on Varian T-60 or A-60 spectrometers. IR spectra were obtained on Perkin—Elmer 337 or Beckman IR-12 spectrometers. Analyses were performed by Galbraith Laboratories.

Preparation of *t*-[PtCl₂(*cis*-CH₃CH=CHOEt)(Py)]

A solution of II (0.40 g, 1.1 mmol) in 10 ml of benzene was stirred with 1 ml (0.7 g, 8 mmol) of *cis*-ethyl propenyl ether for one hour. The solvent was removed at reduced pressure and the yellow solid was vacuum dried, 0.42 g (90% yield) m.p. 120°C. Found: C, 28.78; H, 3.38. C₁₀H₁₅Cl₂NOPt calcd.: C, 27.85; H, 3.51%. Proton NMR (δ (ppm), CDCl₃) 1.53 (t, *J* 7 Hz, CH₂CH₃), 1.69 (td, *J*(Pt—H) 28 Hz, *J*(=CH—CH₃) 6 Hz, CHCH₃), 4.35 (m, CH₂—CH₃), 5.03 (m, =CH—CH₃), 7.23 (td, *J*(Pt—H) 76 Hz, *J*(CH=CH) 4 Hz, O—CH), 7.47 (t, *m*-H), 7.90 (t, *p*-H), 8.83 (td, *J*(Pt—H) 33 Hz, *o*-H).

Preparation of *t*-[PtCl₂(*trans*-CH₃CH=CHOEt)(Py)]

10 ml of benzene containing 0.40 g of II (1.1 mmol) and 0.5 ml (0.35 g, 4 mmol) of *trans*-ethyl propenyl ether was stirred for 18 h. Removal of solvent and vacuum drying gave a yellow solid, m.p. 90°C. Found: C, 27.60; H, 3.50. C₁₀H₁₅Cl₂NOPt calcd.: C, 27.85; H, 3.51%.

Preparation of t -[PtCl₂(*cis*-CH₃CH=CHOEt)(2,4,6-Me₃Py)]

A mixture of t -[PtCl₂(C₂H₄)(2,4,6-Me₃Py)] (0.83 g, 2.0 mmol) and 5 ml of *cis*-ethyl propenyl ether was refluxed for 3 h. Solvent was removed from the clear yellow solution in vacuo and the resulting yellow powder was vacuum dried, m.p. 98–100°C. Proton NMR (δ (ppm), CDCl₃) 1.47 (t, J 7 Hz, CH₂CH₃), 1.67 (td, J (Pt–H) 30 Hz, J 7 Hz, =CHCH₃), 2.33 (3H, s, *p*-Me), 3.23 (6H, t, J (Pt–H) 12 Hz, *o*-Me), 4.35 (2H, m, >CH₂), 4.92 (1H, m, =CHCH₃), 7.00 (3H, s, *m*-H and O–CH=).

Preparation of t -[PtCl₂(C₂H₄)(Et₂NH)] (III)

A solution of KPtCl₃(C₂H₄) (0.92 g, 2.5 mmol) in 30 ml of water was treated with 0.26 ml of diethylamine (2.5 mmol). The reaction mixture was stirred 0.5 h and the yellow precipitate was filtered and washed with 15 ml of water in three portions. Vacuum drying provided 0.73 g (80%), m.p. 99–100°C. Proton NMR (δ (ppm), CDCl₃) 1.57 (6H, t, J 6 Hz, CH₃), 2.3–3.8 (5H, m, >N–CH₂ and >NH), 4.67 (4H, t, J (Pt–H) 61 Hz, =CH₂).

Preparation of t -[PtCl₂(H₂C=CHOEt)(Et₂NH)] (IV)

A solution of III in benzene was treated with excess ethyl vinyl ether. Solvent removal and vacuum drying yielded a yellow solid, m.p. 63°C. Proton NMR (δ , (ppm), CDCl₃) 1.2–1.8 (9H, m, CH₃), 2.1–4.6 (9H, m, CH₂, =CH₂, NH), 7.00 (1H, tdd, J (Pt–H) 64 Hz, J 11 and 4 Hz, O–CH=).

Reaction of diethylamine with IV

Diethylamine (0.21 ml, 2.0 mmol) was added to 0.822 g (2.0 mmol) of IV in 5 ml of benzene. The orange solution was allowed to stand for 24 h. Solvent was removed under reduced pressure, and the yellow-orange powder was recrystallized from CH₂Cl₂/hexane, m.p. 120°C. Found: C, 27.22; H, 5.56; N, 6.50. PtCl₂(H₂C=CHNET₂)(Et₂NH) (C₁₀H₂₄Cl₂N₂Pt) calcd.: C, 27.40; H, 5.52; N, 6.39%. Proton NMR (δ (ppm), CDCl₃) 1.1–1.8 (12H, m, CH₃), 2.3–4.2 (11H, m, CH₂, =CH₂, NH), 7.52 (t, 1H, J 9 Hz, N–CH=). IR (CHCl₃, nujol) 3250w, 3000s, 2950(sh), 2900(sh), 1601vs, 1477m, 1454s, 1388s, 1240s, 1189w, 1152s, 1110m, 1050s, 971s, 928w, 860m, 669m, 542s, 332s.

Alkoxide exchange (typical experiment)

A stock solution was prepared by mixing weighed quantities of ethyl vinyl ether (0.95 ml, 10 mmol), 1-butanol (0.92 ml, 10 mmol) and decane (GLC standard). A solution of II (0.010 g, 0.03 mmol) in 1 ml of the stock solution was allowed to stand at room temperature and monitored by GLC until equilibrium was achieved, Table 1.

Stoichiometric isomerization during displacement of ethyl propenyl ether with pyridine

A solution of t -[PtCl₂(*cis*-CH₃CH=CHOEt)(Py)] (0.086 g, 0.20 mmol) in 1 ml of toluene was treated with 0.13 ml of pyridine (1.6 mmol). The clear yellow solution was allowed to stand at room temperature until precipitation of t -[PtCl₂(Py)₂] was complete. GLC analysis of the colorless supernatant gave a *cis*–*trans* ratio of the liberated ethyl propenyl ether of 1.6/1. Thermodynamic equilibrium is 1.476 [11].

Results under other conditions are:

Mol Py/mol complex	1	1	32	4 *
<i>cis/trans</i>	1.6	1.7	1.6	1.3

The substituted pyridines, 2-MePy, 4-CH₃COPy, and 4-*t*-BuPy were also used for the displacement and isomerization, with approximately the same results as with pyridine.

Preparation of CH₃CD=CHOEt

Propanal-2,2-*d*₂ was obtained by sequential exchange with acidified D₂O, [12]. The labelled propanal (60% D, 25 ml) was treated with 65 ml of EtOD in the presence of 1 ml of 20% DCl [11]. The resulting acetal, CH₃CD₂CH(OEt)₂ (82% D) was treated in 3 g batches with a few crystals of sodium bisulfate [11]. The *cis*- and *trans*-ethyl propenyl ethers were collected with ethanol and unreacted acetal and then separated by GLC. Pure *cis*-ethyl propenyl ether was isolated by GLC of the *cis-trans* mixture. Proton NMR showed 52% D for *cis*-CH₃CD=CHOEt.

Preparation of *t*-[PtCl₂(*cis*-CH₃CD=CHOEt)(Py)] (V)

A solution of II (0.41 g, 1.1 mmol) in 6 ml of benzene was stirred with 0.5 ml of *cis*-CH₃CD=CHOEt (0.38 g, 4.4 mmol) for 3 h. Solvent was removed in vacuo and the yellow solid was vacuum dried, m.p. 117–119°C. Proton NMR established complete replacement of ethylene by propenyl ether.

Displacement of *cis*-CH₃CD=CHOEt from V with pyridine

A solution of 0.35 g of V (0.80 mmol) in 4 ml of toluene was treated with 0.26 ml of pyridine (3.2 mmol). After complete precipitation, the isomerized propenyl ether was isolated by preparative GLC and examined by proton NMR.

Catalytic isomerization of *cis*-(C₆H₅CH=CHOEt)

A solution of II (0.112 g, 0.30 mmol) in 10 ml of dry acetonitrile was heated to 60°C with 0.445 g (3.0 mmol) of *cis*-C₆H₅CH=CHOEt under dry nitrogen. Equilibrium (GLC) was achieved in 22 h.

Catalytic isomerization of *cis*-ethyl propenyl ether

A solution of 0.037 g of II (0.10 mmol) in 10 ml of acetonitrile was refluxed with 0.90 ml (8.0 mmol) of *cis*-ethyl propenyl ether under dry nitrogen. Equilibration (GLC) was achieved in 20 h.

The use of II as a catalyst was dictated in part by its ready availability in this laboratory. It is likely that a wide range of similar complexes may be used as catalysts.

Acknowledgement

We wish to thank Engelhard Industries, Inc. for a generous supply of platinum.

* Starting with *t*-[PtCl₂(*trans*-CH₃CH=CHOEt)(Py)].

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