A plot of ΔS_{eq} vs. ΔH_{eq} (Figure 1) demonstrates that the equilibrium thermodynamic values for palladium(II) phosphole complexes lie well within the range observed for palladium(II) phosphine complexes. The scatter of the points indicates that ΔH_{bond} and ΔS_{free} are important in the thermodynamic process as discussed previously.[19] The information in Figure 1 suggests that the relative energies between the cis and trans isomers for the palladium(II) phosphole complexes are not radically different from those for palladium(II) phosphine complexes. It also supports our contention that these phospholes coordinate as strongly as do phosphines—a prime question at the beginning of our study into the coordination chemistry of these phospholes.

Conductivity studies of these complexes in $CHCl_3$ at 25 °C do not indicate the existence of ionic species in the presence or absence of excess ligand. This would indicate that in $CDCl_3$ the cis–trans isomerization is proceeding through either pathway 3 (eq 1), consecutive neutral ligand displacement, or pathway 2 (pseudorotation of pentacoordinate transition states). Upon addition of excess ligand to the complexes in nitromethane, 1:1 electrolytes are detected in solution, suggesting that in nitromethane or other polar solvents such as nitrobenzene, the isomerization mechanism involves consecutive anion displacement (pathway 1). Since these phospholes are small and seem to have a propensity[30] for π bonding, the likelihood of pentacoordination is greater for the 1-R-3,4-dimethylphospholes than for phosphines in $CHCl_3$, and most likely in benzene as well. The solution behavior in nitromethane further suggests that the Pd–phosphole bond strengths are greater than the Pd–X bond strengths.

Support for the existence of pentacoordinate transition states in $CHCl_3$ comes from the observation that addition of 1:1 excesses of phospholes to their complexes gives rise to single, broad ^{31}P NMR resonances at room temperature, suggesting rapid exchange between free and coordinated phosphole. When the solution is cooled to −50 °C, the broad line is replaced by a complex set of narrow lines, some exhibiting P–P coupling. This suggests the presence of species having increased coordination numbers in solution. The number of lines and temperature behavior of these solutions indicate that an equilibrium between several species is occurring in these solutions. Further studies to elucidate the nature of these species are in progress and will be discussed elsewhere.

Acknowledgment. The financial support of the University of Nevada, Reno, Research Advisory Board and of the National Science Foundation (Grant No. CHE77-08937), which provided funds to purchase the FT NMR spectrometer, is gratefully acknowledged.

Registry No. *cis*-L_2PdX_2 (R = CH_3, X = Cl), 72402-81-4; *cis*-L_2PdX_2 (R = CH_3, X = Br), 72402-85-8; *trans*-L_2PdX_2 (R = CH_3, X = Br), 72442-16-1; *cis*-L_2PdX_2 (R = CH_3, X = N_3), 72402-90-5; *cis*-L_2PdX_2 (R = *n*-Bu, X = Cl), 72402-82-5; *trans*-L_2PdX_2 (R = *n*-Bu, X = Cl), 72937-29-2; *cis*-L_2PdX_2 (R = *n*-Bu, X = Br), 72402-86-9; *trans*-L_2PdX_2 (R = *n*-Bu, X = Br), 72442-17-2; *cis*-L_2PdX_2 (R = *t*-Bu, X = Cl), 72402-83-6; *trans*-L_2PdX_2 (R = *t*-Bu, X = Cl), 72442-15-0; *trans*-L_2PdX_2 (R = *t*-Bu, X = Br), 72442-18-3; *cis*-L_2PdX_2 (R = *t*-Bu, X = N_3), 72402-91-6; *cis*-L_2PdX_2 (R = Ph, X = Cl), 66368-11-4; *trans*-L_2PdX_2 (R = Ph, X = Cl), 72937-30-5; *cis*-L_2PdX_2 (R = Ph, X = Br), 72402-88-1; *trans*-L_2PdX_2 (R = Ph, X = Br), 72442-19-4; *cis*-L_2PdX_2 (R = Ph, X = N_3), 72402-92-7; *cis*-L_2PdX_2 (R = Bzl, X = Cl), 72402-84-7; *cis*-L_2PdX_2 (R = Bzl, X = Br), 72402-89-2; *trans*-L_2PdX_2 (R = Bzl, X = Br), 72442-20-7; *cis*-L_2PdX_2 (R = Bzl, X = N_3), 72402-93-8.

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Reactions of Tetrakis(triphenylphosphine)platinum(0) and (Ethylene)bis(triphenylphosphine)platinum(0) with Strong Proton Acids[1]

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This paper outlines a brief study of the reactions of two soluble platinum(0) complexes—(ethylene)bis(triphenylphosphine)platinum(0) (**1**) and tetrakis(triphenylphosphine)platinum(0) (**2**)—with sulfuric acid and trifluoromethanesulfonic acid (triflic acid). These studies are pertinent to an appreciation of the reactivity of low-valent transition-metal complexes in strongly acidic media and suggest processes which may be important in catalytic oxidation–reduction reactions and hydrogenations in these media.[2]

Results

Reaction of **1** with triflic acid yields ethane as the only volatile product: the yield varies from ca. 70% for heterogeneous reactions between acid and either solid **1** or a heptane slurry of **1** to ca. 30% for homogeneous reaction with a benzene solution of **1** (Scheme I).[3] The reaction is complete in less than 2 min at 0 °C. GLC detects no ethylene in these experiments, but control experiments indicate that ethylene, if produced, would be consumed rapidly by reaction with the strong acid. Dihydrogen was also not detected. Removal of excess triflic acid at the conclusion of a reaction and treatment of the platinum-containing residue with lithium chloride generated dichlorobis(triphenylphosphine)platinum(II) (**3**); we assume that ditriflylbis(triphenylphosphine)platinum(II) is the precursor of this substance.

Qualitatively similar results were obtained on treatment of **1** with sulfuric acid. Treatment of **1** in ether with anhydrous hydrogen chloride generated ethylene and *trans*-hydridochlorobis(triphenylphosphine)platinum(II) (**4**).[3] Reaction of **2** with triflic or sulfuric acid immediately generated dihydrogen (85% yield); reaction of **2** with hydrochloric acid is reported to yield **4** by a path which involves $[(Ph_3P)_3PtH]^+Cl^-$ as an intermediate.[4]

In order to examine the influence of medium acidity on the partitioning of the ethylene moities of **1** between ethane and ethylene, we determined the yield of ethane following reaction in sulfuric acid–tetrahydrofuran mixtures. Typical results are summarized in Figure 1. Ethane generation requires a very strongly acidic medium: in mixtures containing less than 70% w:w H_2SO_4 (1.75 mol of H_2SO_4 to 1 mol of THF), no significant yield of ethane is produced. At these lower acidities, the reaction of ethylene with sulfuric acid is relatively slow, and ethylene is readily detected, although the observed yields are only qualitative. Isotopic-exchange experiments carried out at high and low acidities are pertinent to the mechanism of ethane production. Ethane produced by reaction of solid **1** with deuterated acids was polydeuterated: from CF_3SO_3D, 27% d_6, 32% d_5, 22% d_4, 15% d_3, 4% d_2; from 100% D_2SO_4, 38% d_6, 32% d_5, 14% d_4, 10% d_3, 6% d_2. Ethane itself does not exchange hydrogen for deuterium with D_2SO_4 (99% D)

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(1) Supported by the National Science Foundation, Grant 771282 CHE.

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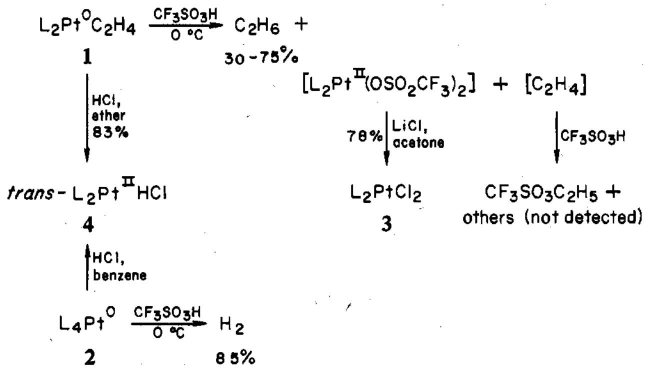
Scheme I. Reactions of Platinum(0) Complexes with Protic Acids (L = Triphenylphosphine)



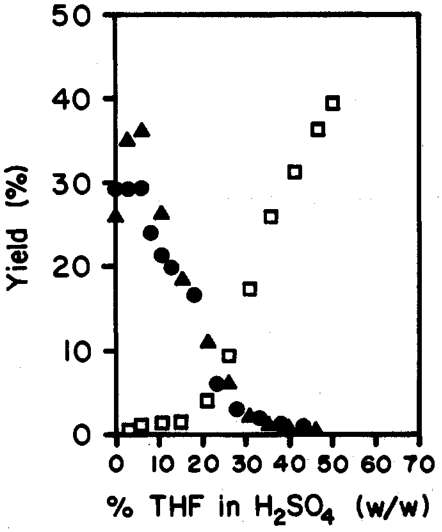


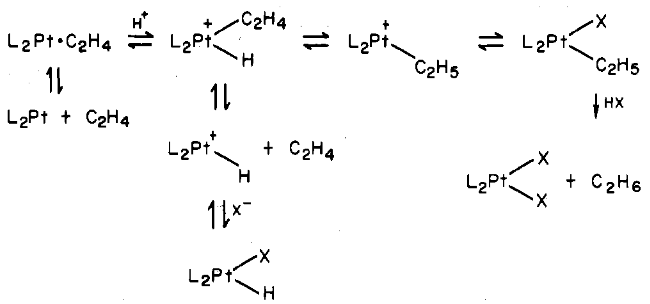
Figure 1. Yields of ethane (●, ▲; two separate experiments) and ethylene (□) formed on protonation of 1 in H_2SO_4/THF solutions. The data given for ethylene should be considered minimum yields since ethylene reacts with sulfuric acid under conditions similar to those encountered in these reactions.

under these conditions.[5] Ethylene recovered from reaction of 1 with 50% D_2SO_4/THF (w/w) (40% yield) was also deuterated: 4% d_4, 10% d_3, 19% d_2, 29% d_1, 38% d_0. Control experiments established that no hydrogen–deuterium exchange occurred between ethylene and this D_2SO_4/THF mixture, either with or without $L_2Pt^{II}(OSO_2CF_3)_2$ present, under the conditions used in reactions of 1.

Qualitative evidence for reversible ethylene loss from 1 or a derivative of 1 during reaction was obtained by carrying out the reaction in the presence of added ethylene. When a solution of 1 in benzene was treated with triflic acid, the yield of ethane was 30%. A similar solution of 1 in benzene saturated with ethylene yielded 60% ethane on the basis of 1 under the same reaction conditions. Ethylene added to a solution of 1 in benzene after complete reaction yielded ethane at an insignificant rate under these conditions (5–10% over 3 h, based on platinum). Thus the increase in the ethane yield from protolysis of 1 in the presence of ethylene is not the result of an independent reduction taking place after the disappearance of 1.

A plausible intermediate in the reaction of 1 with triflic acid is $(Ph_3P)_2PtH(O_3SCF_3)$ (**5**). We generated a material which we believe to be **5** in situ by treatment of $(Ph_3P)_2PtHCl$ with silver triflate. Reaction of this substance with triflic acid produced dihydrogen, howbeit in only ca. 40% yield.

Scheme II. Plausible Mechanism for Generation of Ethane by Reaction of 1 with Acids



Discussion

The principal conclusion of this study is that 1 is a sufficiently strong reducing agent in strongly acidic media to convert ethylene to ethane and that 2 is sufficiently reducing to generate dihydrogen. Scheme II presents a plausible pathway for conversion of 1 to ethane and a bis(triphenylphosphine)platinum(II) derivative. The observations of deuterium exchange in recovered ethylene and product ethane are consistent with the hypothesis that both ethylene dissociation from platinum (from one or several possible species, including $L_2Pt^0{\cdot}C_2H_4$, $[L_2Pt^{II}H{\cdot}C_2H_4]^+$, and $L_2Pt^{II}HX{\cdot}C_2H_4$) and interconversion of hydrido(ethylene)platinum(II) and ethylplatinum(II) intermediates[6] are equilibria occurring rapidly before the rate-limiting generation of ethane by protolytic cleavage of the carbon–platinum bond of an ethylplatinum species.[7] The fact that ethane is observed only in very strongly proton-donating media, while acid-promoted release of ethylene occurs in considerably less acidic media, is consistent with this hypothesis. There are clearly many equilibria involving association of triflate or bisulfate ions with platinum intermediates which should be considered in a complete description of these reactions; we do not have the evidence required to comment on them.

Reactions of 1 and 2 with triflic acid are rapid and appear to result in complete oxidation of platinum(0). The products detected (for 1, 30–75% ethane but, apparently, no dihydrogen; for 2, 85% dihydrogen) do not provide a satisfactory accounting for the reducing equivalents consumed. Some element of experimental artifact may be involved: small quantities of dihydrogen were not easy to detect by the procedure used in these experiments. It is, however, probable that some presently unidentified components of the reaction mixtures are acting as oxidizing agents.[8] The detection of only a modest yield (40%) of dihydrogen from 5 on treatment with triflic acid is compatible with this suggestion. These observations suggest

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(5) Conditions for H–D exchange of hydrocarbons by Pt(II) salts in acid media are generally severe: 100 °C for 18 h with 10% D incorporation. Hodges, R. J.; Webster, D. E.; Wells, P. B. *J. Chem. Soc. A* **1971**, 3230–8. Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174–5.

(6) These intermediates were observed in similar systems. Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1972**, *11*, 1275–80. Kemmitt, R. D. W.; Kimura, B. Y.; Littlecott, G. W.; Moore, R. D. *J. Organomet. Chem.* **1972**, *44*, 403–9. Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 203–9. Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669–76. Giustiniani, M.; Dolcetti, G.; Pietropaolo, R.; Belluco, U. *Inorg. Chem.* **1969**, *8*, 1048–51.

(7) An effort to infer the stereochemistry of addition of the elements of dihydrogen to the ethylene group of 1 by examining the stereochemistry of corresponding reduction of the olefinic group of (norbornene)bis(triphenylphosphine)platinum(0) in CF_3SO_3D was frustrated by the production of extensively polydeuterated norbornane. In this instance, reduction of norbornene to norbornane occurred in triflic acid even in the absence of platinum(0).

(8) Triflic acid is commonly considered to be a nonoxidizing acid, but it may be acting as an oxidizing agent under these circumstances. The aromatic rings and the phosphorus–carbon bonds of the triphenylphosphine groups are also, in principle, susceptible to reduction. Other potential oxidants are also present.

that further, possibly interesting, redox chemistry is taking place in these systems, but we have not explored this chemistry further.

The relevance of these studies for catalysis lies in the observation that even nonoxidizing acids having conjugate bases which coordinate weakly with platinum (II) are capable of oxidizing platinum(0) to platinum (II), provided that the hydrogen ion activity of the medium is sufficiently high. At pH $\simeq 7$, **2** is unprotonated; between pH $\simeq 2$ and $H_0 \simeq -10$, **2** exists as $(Ph_3P)_3PtH^+$; at $H_0 < -10$, **2** reacts and generates dihydrogen. Although these estimates of ranges are very approximate, they provide evidence that redox chemistry involving metals and hydrogen ions in very strongly acidic media may be qualitatively different from that in weaker acids.

Experimental Section

General Methods. Reactions involving organometallic compounds were carried out by using standard inert atmosphere techniques.[9] THF was distilled from disodium benzophenone anion, and benzene from P_2O_5. Preparations of trifluoromethanesulfonic anhydride,[10] trifluoromethanesulfonic acid-*d*,[10] 100% sulfuric acid,[11] **1**,[12] and **2**[13] followed literature procedures. Silver triflate (99%, Ventron), triflic acid (3M Co.), and D_2SO_4 (Columbia Chemicals Co.) were used as purchased.

Hydrogen analyses were carried out by measuring evolved gas volumes on a vacuum line. Reaction was carried out on the line, and the volume of gas which was not condensed at −196 °C was taken to be that of dihydrogen. The working volume of the line was calibrated by using known quantities of dihydrogen generated by reaction of magnesium metal with an excess of 50% aqueous sulfuric acid. In certain instances these analyses were confirmed by measuring evolved gas volumes over water and identifying dihydrogen by mass spectroscopy.

Reactions of 1 with Acids: General Procedures. An argon-filled flask equipped with a side arm was charged with **1** (~ 0.3 mmol). Acid (~1 mL) was placed in the side arm, and the flask capped with a No-Air stopper. The apparatus was connected to a water-filled gas buret by a cannula, the acid added to the **1**, and the volume of evolved gas measured. The gas was identified as ethane by GLC. To identify the platinum-containing product from **1** and triflic acid, the excess triflic acid was removed under vacuum (0.005 torr). The residue was treated with 0.1 g of lithium chloride and 30 mL of acetone. The resulting mixture was allowed to stir for 0.5 h and then worked up by washing with water (2 × 15 mL) and recrystallization from ethylene chloride–heptane. The $(Ph_3P)_2PtCl_2$ had mp 310–312 °C dec (lit.[14] mp 310 °C dec) and IR and ^{31}P NMR spectra indistinguishable from authentic material.

Reactions of 2 with Acids: General Procedures. A flask containing the platinum compound (either as a solid or a solution, 0.6 mmol) and having the acid (1 mL) in a side arm was attached to the vacuum line and evacuated to 0.005 torr. The acid was added to 0 °C, and the volume of the evolved gas measured.

The reaction of **1** with acids was also carried out in benzene solution, and the ethane produced analyzed by GLC using cyclopentane as internal standard. Parallel analysis by expansion in a calibrated vacuum line yielded similar results. The IR spectrum of the gas (10-cm gas cell) was indistinguishable from authentic ethane. The isotopic composition of the mixture of deuterated ethanes produced on reaction of **1** with deuterated acids was analyzed by using fragmentation patterns from the literature.[15]

Reactions of 1 with THF–H_2SO_4 Mixtures. Colorless solutions of H_2SO_4 in THF were made by successive dilutions of 100% H_2SO_4 with THF at 0 °C. Aliquots (0.1 mL) of each solution were immediately mixed with benzene solutions of **1**. The quantity of ethane produced was measured relative to a propane internal GLC standard. The yield of ethane had reached its maximum value in 2 min and did not change in the following 4 h.

Preparation and Reaction of 5. In a dry, argon-filled 200-mL one-necked flask was placed *trans*-$(Ph_3P)_2PtHCl$ (0.427 g, 0.567 mmol) and 50 mL of methylene chloride. The solution was stirred vigorously by using a magnetic stirring bar, and silver triflate (0.15 g, 0.56 mmol, partially soluble) was added. After 2 h, the solution was separated from silver chloride (0.078 g, 0.55 mmol) by centrifugation. The solution was concentrated under vacuum, leaving an off-white solid. An attempt to obtain an NMR spectrum of this material in C_6D_6 was unsuccessful: **5** appeared to react with the benzene. A sample of **5** (0.319 g, 0.37 mmol) was treated with 1 mL of triflic acid: a quantity of gas (uncondensable at −196 °C and 0.005 torr) corresponding to a 37% yield of dihydrogen was released.

Registry No. **1**, 12120-15-9; **2**, 14221-02-4; **3**, 10199-34-5; **4**, 16841-99-9; **5**, 72926-39-7.

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Cis–Trans Isomerism in (trpy)$(PPh_3)RuCl_2$. Comparisons between the Chemical and Physical Properties of a Cis–Trans Isomeric Pair

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Although cis–trans isomerism in octahedral metal complexes is a common occurrence, there are relatively few studies defining the contrasting chemical and physical properties of a cis–trans pair, especially of the second- and third-row transition metals. We report here the synthesis of complexes derived from the planar, tridendate ligand 2,2′,2″-terpyridine (trpy) of the type (trpy)$Ru^{II}(L)Cl_2$ (L = PPh_3, $P(p\text{-}C_6H_4Me)_3$, pyridine). The syntheses are based on the synthetically useful precursor complex (trpy)$RuCl_3$. Also reported are some rather striking differences in the properties of the cis and trans isomers of the phosphine derivatives.

Experimental Section

Measurements. Ultraviolet, visible, and near-infrared spectra were recorded by using either a Cary Model 14 or Bausch and Lomb Model 210 spectrophotometer. Molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. Proton and ^{31}P NMR spectra were recorded on a Varian 10-MHz Fourier transform spectrometer with Me_4Si as an internal standard for protons and 15% H_3PO_4 in D_2O as an external standard for phosphorus. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) at 23 ± 2 °C and are uncorrected for junction potential effects. The $E_{1/2}$ values for the reversible couples were calculated from half the difference between E_p values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are used as formal reduction potentials, assuming differences in diffusion coefficients for oxidized and reduced species are negligible. The measurements were made by using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetry measurements. Values for *n*, where *n* is the total number of electrons transferred per complex in an exhaustive oxidative electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. The reactions were considered complete after the current had fallen to 1% of the initial value. Values of *n* for the rereduction of the oxidized product were determined by the same criterion. All coulometry measurements were performed at platinum screen electrodes using MCB Spectrograde acetonitrile as the solvent and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the electrolyte. Elemental analyses were

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