

Preparation of Hydrides by Protonation of Tetrakis(triphenylphosphine)platinum(0) with Carboxylic Acids¹

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The preparation of the series of complexes $[(PPh_3)_3PtH]X$ by protonation of $(PPh_3)_4Pt$ is described, where X is $(CF_3COO)_2H$, $(CF_2ClCOO)_2H$, $(C_2F_5COO)_2H$, $(CF_3COO)_2H$, or $(COO)_4H$. The 1H nmr spectrum in the hydride region shows a pair of double doublets for the center lines and two pairs of triplets for the ^{195}Pt satellites. This difference is discussed in relation to second-order effects, which probably causes the center line of the spectrum of the ion $[(PPh_3)_3PtH]^+$ to appear as a double doublet. When PPh_3 is added to a solution of $[(PPh_3)_3PtH](CF_3COO)_2H$, the cis phosphines undergo exchange and the center line of the 1H nmr spectrum appears as a sharp doublet ($J_{P(Trans)-H} = 160$ Hz). When $PMePh_2$ or PMe_2Ph is added, both the cis and trans phosphines are involved in the exchange, and the resonance appears as a sharp singlet. The conductivity of $[(PPh_3)_3PtH](CF_3COO)_2H$ in nitrobenzene is $22.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$, which increases to $28.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ after the addition of 1 mol of PPh_3 . Further addition of PPh_3 causes no significant increases in the conductivity.

In a recent publication² we reported that acetic acid would oxidatively add to $(PPh_3)_4Pt$ to give a hydride complex which on attempted isolation readily dissociated back into $(PPh_3)_3Pt$ and CH_3COOH . Although the 1H nmr in the hydride region confirms protonation on the metal, the spectrum is of further interest since there is a splitting of 160 Hz due to a triphenylphosphine in a trans position to the hydride³ but coupling due to the cis triphenylphosphines cannot be observed. In view of the lability of this system, we decided to further study the protonation of platinum(0) complexes with carboxylic acids. An additional aspect of this chemistry which we wished to examine is the role played by hydride complexes of platinum(IV) as intermediates in protonation reactions of zerovalent platinum. In a related study we have proposed such an intermediate species in the reaction of complexes of the type $(PPh_3)_2Pt(\text{acetylene})$.⁴ Platinum(IV) dihydrides have been reported synthesized by the protonation of $(Et_3P)_2PtHCl$ with HCl ⁵ and the reaction between $(PPh_3)_4Pt$ and 1-ethynylcyclohexanol.⁶ In addition, the platinum(IV) dihydride complex, $(PPh_3)_2PtH_2Cl_2$, has been postulated,⁷ but we have recently shown that the existence of this compound is in doubt.⁸ Nevertheless, dihydrides of the type $(PPh_3)_2PtH_2X_2$ are of interest because of observations that protonation of $(PPh_3)_4Pt$ by HX may lead to formation of $(PPh_3)_2PtX_2$ ⁹⁻¹¹ rather than the monohydride. Hence, we consider that a platinum(IV) dihydride is a plausible intermediate in such reactions since it can undergo reductive

elimination to form either the platinum(II) hydride $trans-(PPh_3)_2PtHX$ or the platinum(II) bis complex $(PPh_3)_2PtX_2$.

Experimental Section

Carbon and hydrogen analyses were carried out by Chemalytics Inc., Tempe, Ariz., and the phosphorus and fluorine analyses by A. Bernhardt, Mullheim-Ruhr, Germany. Molecular weight data were obtained by Galbraith Laboratories Inc., Knoxville, Tenn. The platinum analysis was carried out by neutron activation analysis making use of the ^{195}Pt isotope ($t_{1/2} = 31$ min with a γ emission of 542.7 keV). The irradiation was carried out for ca. 10 min and the samples were allowed to decay for 4 half-lives before counting the spectra. Nuclear magnetic resonance spectra were obtained on Varian A-60, T-60, and HA-100 spectrometers using TMS as internal reference. Infrared spectra were obtained as Nujol mulls and $CHCl_3$ solutions on a Perkin-Elmer Model 700 spectrometer. Melting points were obtained on a microscope hot stage and are uncorrected. Conductivity measurements on $1.00 \times 10^{-3} M$ solutions were obtained with an Industrial Instruments Model 16 B 2 conductivity bridge using platinum electrodes. The nitrobenzene (J. T. Baker) was dried and vacuum distilled twice before use and had a resistance of more than 2×10^6 ohms. The cell constant was determined with $1.000 M$ KCl solution prior to use. Potassium tetrachloroplatinate was obtained from Engelhard Industries Inc. Triphenylphosphine was obtained from Carlisle Chemicals and recrystallized from ethanol before use. $(PPh_3)_2Pt(C_2H_4)$ was prepared by the previously described method.¹² All reactions were carried out under an atmosphere of nitrogen or argon. Computer simulations of 1H nmr spectra were carried out using a LAOCOON III program.

trans-Hydridotrifluoroacetatobis(triphenylphosphine)platinum(II). Method A.—A solution of $[(PPh_3)_3PtH](CF_3COO)_2H$ (1.00 g) in pyridine (20 ml) was stirred for 1.5 hr. A mixed solution of hexane (400 ml) and ether (50 ml) was added to this pyridine solution to give a brown precipitate. This was recrystallized three times from $CHCl_3$ to give the complex as pale cream crystals, mp 202° dec; yield 75%; $\nu_{C=O}$ 1692 cm^{-1} , ν_{Pt-H} 2295 cm^{-1} , τ_{Pt-H} 31.2; molar conductance $1.5 \text{ ohm}^{-1} \text{ cm}^2$. Anal. Calcd for $C_{38}H_{31}F_3O_2P_2Pt$: C, 54.8; H, 3.75; mol wt 834. Found: C, 54.4; H, 3.81; mol wt 833 (benzene).

Method B.—To a solution of $(PPh_3)_2Pt(C_2H_4)$ (300 mg) in benzene (7 ml) was added CF_3COOH (0.2 ml) and the mixture was stirred for 15 min. This benzene solution was then added to hexane (50 ml) and the brown solid which formed was filtered. This solid was then recrystallized twice by dissolving in CH_2Cl_2 and then adding a 1:8 mixture of ether and hexane to give the complex as crystals; yield 90%.

Hydridotris(triphenylphosphine)platinum(II) Hydrogen Bis(trifluoroacetate).—To a filtered solution of $(PPh_3)_4Pt$ (480 mg) in benzene (20 ml) was added CF_3COOH dropwise until the

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yellow color of the solution just disappeared. This benzene solution was then added to a 1:3 mixture of ether and hexane to give a white precipitate. Two recrystallizations from CH_2Cl_2 by addition of the 1:8 hexane mixture gave the complex which was dried *in vacuo*, mp 132° dec; yield 87%; $\nu_{\text{C=O}}$ 1780 cm^{-1} , $\nu_{\text{Pt-H}}$ 2145 cm^{-1} , $\nu_{\text{Pt-H}}(\text{CHCl}_3)$ 2145 cm^{-1} , $\tau_{\text{Pt-H}}$ 15.83, $\tau_{\text{O-H}}$ -3.7; molar conductance 22.4 $\text{ohm}^{-1} \text{cm}^2$. *Anal.* Calcd for $\text{C}_{38}\text{H}_{47}\text{F}_8\text{O}_4\text{P}_3\text{Pt}$: C, 57.6; H, 3.92; F, 9.54; P, 7.68; Pt, 16.12; mol wt 1210. Found: C, 57.7; H, 3.82; F, 9.42; P, 7.55; Pt, 16.17; mol wt 1295 (CHCl_3). The complex is extremely soluble in CH_2Cl_2 and solutions of up to 0.6 M can be prepared.

Hydridotris(triphenylphosphine)platinum(II) Hydrogen Bis(chlorodifluoroacetate).—Using the same procedure as for the trifluoroacetate compound, the complex was obtained as colorless crystals which were dried *in vacuo*, mp 138° dec; yield 85%; $\nu_{\text{C=O}}$ 1780 cm^{-1} , $\nu_{\text{Pt-H}}$ 2150 cm^{-1} , $\nu_{\text{Pt-H}}(\text{CHCl}_3)$ 2145 cm^{-1} , $\tau_{\text{Pt-H}}$ 15.82, $\tau_{\text{O-H}}$ -7.8; molar conductance 22.5 $\text{ohm}^{-1} \text{cm}^2$. *Anal.* Calcd for $\text{C}_{38}\text{H}_{47}\text{Cl}_2\text{F}_8\text{O}_4\text{P}_3\text{Pt}$: C, 56.0; H, 3.81; Cl, 5.70; F, 6.11; mol wt 1243. Found: C, 56.4; H, 3.66; Cl, 5.80; F, 5.75; mol wt 1200 (CHCl_3).

Hydridotris(triphenylphosphine)platinum(II) Hydrogen Bis(pentafluoropropionate).—Again using the same procedure as for the trifluoroacetate compound, the complex was obtained as colorless crystals which were dried *in vacuo*, mp 115° dec; yield 40%; $\nu_{\text{C=O}}$ 1780 cm^{-1} , $\nu_{\text{Pt-H}}$ 2140 cm^{-1} , $\nu_{\text{Pt-H}}(\text{CHCl}_3)$ 2145 cm^{-1} , $\tau_{\text{Pt-H}}$ 15.83, $\tau_{\text{O-H}}$ -5.2; molar conductance 22.1 $\text{ohm}^{-1} \text{cm}^2$. *Anal.* Calcd for $\text{C}_{60}\text{H}_{47}\text{F}_{10}\text{O}_4\text{P}_3\text{Pt}$: C, 55.0; H, 3.62; F, 14.5; P, 7.09; mol wt 1310. Found: C, 54.8; H, 3.46; F, 14.4; P, 6.61; mol wt 1112.

Hydridotris(triphenylphosphine)platinum(II) Hydrogen Perfluorosuccinate.—A solution of perfluorosuccinic acid was made up containing 100 mg of the acid dissolved in ether (1 ml). The acid solution was added dropwise to a filtered solution of $(\text{PPh}_3)_4\text{Pt}$ (500 mg) in benzene (25 ml) until the yellow color was just discharged. The mixture was stirred for 10 min and then poured into a 1:90 mixture of ether and hexane. The colorless solid was collected and recrystallized twice from CH_2Cl_2 by addition of the ether-hexane mixture to give the complex as colorless crystals which were dried *in vacuo*, mp 192° dec; yield 84%; $\nu_{\text{C=O}}$ 1600 cm^{-1} , $\nu_{\text{Pt-H}}$ 2090 cm^{-1} , $\nu_{\text{Pt-H}}(\text{CHCl}_3)$ 2145 cm^{-1} , $\tau_{\text{Pt-H}}$ 15.83, $\tau_{\text{O-H}}$ -7.5; molar conductance 28.7 $\text{ohm}^{-1} \text{cm}^2$. *Anal.* Calcd for $\text{C}_{58}\text{H}_{47}\text{F}_4\text{O}_4\text{P}_3\text{Pt}$: C, 59.4; H, 4.04; F, 6.48. Found: C, 58.6; H, 3.77; F, 6.43.

Hydridotris(triphenylphosphine)platinum(II) Trihydrogen Di-oxalate.—To a filtered solution of $(\text{PPh}_3)_3\text{Pt}$ (100 mg) in a mixture of benzene (5 ml) and CH_2Cl_2 (5 ml) was added oxalic acid (80 mg). The solution was vigorously stirred until the yellow color was discharged (*ca.* 10 min). The solution was filtered and poured into hexane (50 ml) to give a colorless solid. Two recrystallizations by dissolution in CH_2Cl_2 , followed by the addition of hexane, gave the pure complex which was dried *in vacuo*, mp 81° dec; yield 68%; $\nu_{\text{C=O}}$ 1710 cm^{-1} , $\nu_{\text{Pt-H}}$ 2110 cm^{-1} , $\nu_{\text{Pt-H}}(\text{CHCl}_3)$ 2145 cm^{-1} , $\tau_{\text{Pt-H}}$ 15.83, $\tau_{\text{O-H}}$ -1.6; molar conductance 21.3 $\text{ohm}^{-1} \text{cm}^2$. *Anal.* Calcd for $\text{C}_{38}\text{H}_{49}\text{O}_8\text{P}_3\text{Pt}$: C, 60.0; H, 4.25; P, 8.00. Found: C, 60.4; H, 4.23; P, 7.50.

Results and Discussion

Although tetrakis(triphenylphosphine)platinum(0) reacts with acetic acid to form a hydride which is difficult to isolate, the reaction of the zerovalent complex with trifluoroacetic acid yields a complex which can be readily obtained in a pure state. The stoichiometry of the compound shows that two molecules of trifluoroacetic acid have added to each $(\text{PPh}_3)_3\text{Pt}$ group and, for reasons to be discussed, we consider the complex to have the formula $[(\text{PPh}_3)_3\text{PtH}](\text{CF}_3\text{COO})_2\text{H}$. This compound appears to be the only product which can be obtained from this reaction. Such a result does not seem to follow previously reported⁷ behavior in these syntheses since the covalent hydride $(\text{PPh}_3)_2\text{PtHX}$ is expected to be formed by reaction in a nonpolar medium, and the ionic hydride $[(\text{PPh}_3)_3\text{PtH}]\text{X}$ by reaction in a polar medium. In order to obtain the covalent hydride by a protonation reaction between trifluoroacetic acid and a Pt(0) complex we have found it necessary to use

$(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ as the starting compound rather than $(\text{PPh}_3)_4\text{Pt}$. We have carried out the reaction between $(\text{PPh}_3)_4\text{Pt}$ and the carboxylic acids CF_2ClCOOH , $\text{C}_2\text{F}_5\text{COOH}$, $(\text{CF}_2)_2(\text{COOH})_2$, and $(\text{COOH})_2$. In each case the ionic hydride is the only product and, with the exception of the perfluorosuccinic acid complex, the anion is a dimeric species.

The reaction with formic and acetic acids yields a hydride in solution as evidenced by a resonance in the ^1H nmr spectrum to high field of TMS. However, attempted isolation leads to an apparent reductive elimination reaction to re-form $(\text{PPh}_3)_3\text{Pt}$ and the carboxylic acid. The formic acid complex appears to be the more stable since we can obtain it as a colorless solid at room temperature; however, when this product is dissolved in CH_2Cl_2 , the color of the solution rapidly changes to yellow, indicative of $(\text{PPh}_3)_3\text{Pt}$. The acetic acid complex can be obtained as a colorless solid at -50° but changes into a tar at 0° . In neither case have we been able to obtain the complexes sufficiently pure for microanalysis. Similarly with both pentafluorobenzoic acid and aqueous HF, we have been able to show the presence of a hydride complex in solution by ^1H nmr but have not succeeded in obtaining an analytically pure compound.

Integration shows that the complexes obtained in these reactions are to be regarded as Pt(II) monohydrides, even though the stoichiometry of the product suggests that two molecules of acid undergo oxidative addition to form a Pt(IV) dihydride. This integration can be carried out in a manner similar to that previously described,⁸ where a mixed solution is used which contains known quantities of the complex and hexamethylbenzene. Furthermore, we have observed the acid proton in the ^1H nmr at a position approximately 13 ppm downfield of TMS, and integration of acid-hydride moieties present is close to that required for a 1:1 ratio. The downfield resonance shows the expected behavior of an acid hydrogen in that its position is sensitive both to changes in concentration and to the presence of added D_2O . The oxalic acid complex can be isolated in a pure state and is surprisingly stable to dissociation back to $(\text{PPh}_3)_3\text{Pt}$. The analytical data show the stoichiometry to be analogous to that of the fluoro complexes with two acid molecules to each platinum, and the spectral data are also closely similar. Even though CF_2ClCOOH forms the complex $[(\text{PPh}_3)_3\text{PtH}](\text{CF}_2\text{ClCOO})_2\text{H}$ in good yield, the reaction with CCl_3COOH is quite different since chlorination on the platinum occurs, and the complex *trans*- $(\text{PPh}_3)_2\text{PtHCl}$ is obtained with no evidence for the formation of $[(\text{PPh}_3)_3\text{PtH}](\text{CCl}_3\text{COO})_2\text{H}$.

Structural Studies.—The infrared spectra of these complexes show the expected band due to $\nu_{\text{Pt-H}}$ in the 2100- cm^{-1} region and the low energy of this band shows that the hydride is *trans* to a group of high *trans* influence^{2,3} such as triphenylphosphine.

Using a first-order approximation, the high-field ^1H nmr spectrum of $[(\text{PPh}_3)_3\text{PtH}]^+$ would be expected to correspond to the X portion of an AB_2X spin system and to show a large splitting of 160–170 Hz due to coupling with the *trans* PPh_3 in the plane and further splitting into triplets from the *cis* PPh_3 groups. The spatial configuration of the ion and the anticipated spectrum are shown in Figure 1 where the *cis* triphenyl-

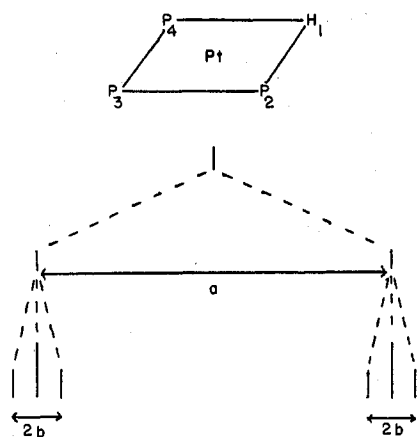


Figure 1.—Representative structure for P_3PtH showing the notation used in presenting the coupling constant data and sketching the first-order spectrum for the X portion ($a = J_{P_2-H_1}$ and $b = J_{P_3-H_1} = J_{P_4-H_1}$). The lines due to coupling with ^{195}Pt are not shown.

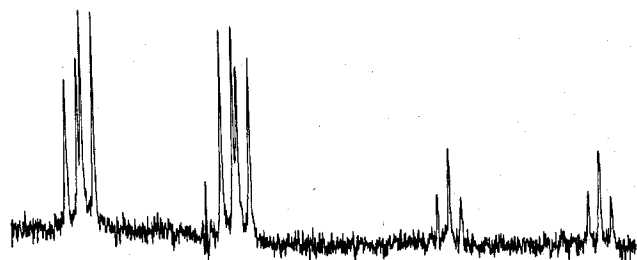


Figure 2.—The 1H nmr spectrum of $[(PPh_3)_3PtH](CF_3COO)_2H$ at 100 MHz (the low-field ^{195}Pt satellites are not shown).

phosphines are labeled P_2 and P_4 and can be regarded as chemically and magnetically equivalent. The spectrum obtained at 100 MHz is shown in Figure 2, and it can be clearly seen that the two center multiplets appear as double doublets rather than triplets. In order to adopt a first-order analysis for the center lines, we must assume nonequivalence of P_2 and P_4 , and then analysis of these lines yields separate values of 13 and 17 Hz for $J_{P_2-H_1}$ and $J_{P_4-H_1}$. This would give a spectrum closely analogous to that of (diphos)PtH(PEt₃)Cl in which one of the nonequivalent cis groups is triethylphosphine while the other is one of the coordinated phosphorus atoms of 1,2-bis(diphenylphosphino)ethane.¹⁸ In the present case, a possible structure in which the cis PPh_3 groups are nonequivalent is a penta-coordinate square pyramid with the trifluoroacetate in the plane of the square and one of the triphenylphosphines cis to the hydride being distorted toward the apical position. Such a structure agrees with the molecular weight and 1H nmr data. However, the compound resembles an ionic hydride in giving a conducting solution in nitrobenzene or dichloromethane, and we decided, therefore, to investigate the system in greater detail.

In nitrobenzene solution, the conductivity of the complex is nearly the same as that for either $NaBPh_4$ or $[(PPh_3)_3PtH]BPh_4$ under the same conditions, and yet the high-field 1H nmr spectrum remains the same in these media as in other solvents. Furthermore, although the complex with aqueous HF is difficult to

isolate pure, the 1H nmr spectrum of a dichloromethane solution of the compound is identical with the one shown in Figure 2 and shows no additional coupling due to $^{19}F-H$ which would be expected if there was any s character in the Pt-F bond. Also, the ir spectra of $CHCl_3$ solutions of all the complexes show the band due to ν_{Pt-H} at 2145 cm^{-1} . This evidence suggests the presence of $[(PPh_3)_3PtH]^+$ in solution, and it is difficult to conceive how P_2 and P_4 are not isochronous, unless the distortion toward the square-pyramidal structure is caused by ion association.

Structural inferences from the 1H nmr spectrum (Figure 2) are further complicated by the fact that the spectrum in the ^{195}Pt satellites appears as triplets rather than as double doublets.¹⁴ This means that analysis of the ^{195}Pt portion of the spectrum corresponds to the anticipated spectrum for P_2 and P_4 being isochronous and magnetically equivalent. Further inspection reveals that the widths of the center-line multiplets are different from those of the satellites, the separation in the triplets being 26 Hz, whereas that within the double doublets is 30 Hz. There is also a discrepancy in the observed coupling of P_3 with the hydride since J_{P_2-H} is 160 Hz in the satellites and 164 Hz in the center-line bands. Cases of the satellites being different are rare for Pt complexes but there have been such reports for exchange systems where the difference is due to nonequivalent hydrogen atoms undergoing exchange at different rates.¹⁵ This explanation does not seem to be useful for this case since the spectrum is due to only a single hydrogen.

In an attempt to understand better these unusual features in the 1H nmr spectrum, we have used a computer technique to simulate the spectra. We did not include any couplings due to the fluorine of the trifluoroacetate because the ^{19}F nmr spectrum showed only a single sharp resonance 76.3 ppm upfield of CCl_3F with no evidence for coupling with the H or P nuclei. The model used is an AB_2X spin system (square planar with $X = H_1$, $A = P_3$, $B = P_2 = P_4$) and it is the X portion of the spectrum which is being considered. Although the complex is quite soluble in chlorinated solvents, the ^{31}P nmr spectrum shows only one line centered 26.6 ppm upfield of ortho phosphoric acid. Since this line is of the order of 40 Hz wide under optimum resolution, it is probable that it is due to P_2 and P_4 , and the coupling of P_3 into a doublet ($J_{P_3-H_1} = 164\text{ Hz}$) causes it to be too weak to be observed. In the calculations we have used data available from the 1H spectrum, along with reasonable values for the chemical shifts and coupling constants of the phosphorus nuclei taken from the literature.¹⁶⁻¹⁹ The lack of complete data from the experimental spectra has made it too involved to obtain an exact fit of all 20 lines in the 1H spectrum but several interesting effects have

(14) (a) The entire spectrum is the same if $CHCl_3$, nitrobenzene, CH_2Cl_2 , or CF_3COOH is used as the solvent, but the resolution of the double doublets is enhanced in the former cases if several drops of CF_3COOH are added to the solvent. (b) In ref 13 the ^{195}Pt satellites are double doublets like the center-line bands.

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been found which we believe give a reasonable explanation of many of its features.²⁰

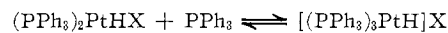
An exact fit of the eight center lines can be obtained in the AB₂X case using the values $J_{1-2} = J_{1-4} = 17$ Hz and $J_{1-3} = 160$ Hz and a difference of 10 Hz between the chemical shifts of the cis and trans phosphorus nuclei. If coupling with ¹⁹⁵Pt is introduced, the calculated AB₂MX spectrum reveals several novel effects. The four groups of satellite multiplets collapse, and the separations now correspond to that of a triplet rather than the double doublets which were found in the AB₂X case. The only part which does not agree with the observed spectrum is the separation within the triplets in the satellites, which is 34 Hz rather than 26 Hz. The coupling constant J_{1-3} is 160 Hz in the AB₂MX case, which is in agreement with the observed values in the satellites. If the values $J_{1-2} = J_{1-4} = 13$ Hz are used, the calculated spectrum exactly matches the observed positions and separations in the satellite resonances, but the center lines are now somewhat converged and do not precisely match. Of primary importance in these results is the fact that a double-doublet splitting pattern may be obtained with the AB₂X case, whereas a triplet splitting pattern may be obtained in the AB₂MX case by simply allowing for coupling with ¹⁹⁵Pt between the various nuclei. Although we cannot achieve an exact fit of the entire spectrum, we believe that such considerations as those discussed above offer a better explanation of these differences in portions of the spectrum than effects such as variations in coupling constants through the different Pt isotopes.

A fit of the center lines can also be obtained for the ABCX case using the values of 13 and 17 Hz for J_{1-2} and J_{1-4} and 164 Hz for J_{1-3} , but inclusion of ¹⁹⁵Pt in the ABCMX case did not give a close fit for the satellites. Although it is likely that the double doublets arise because of second-order effects, we cannot discount the ABCX case where the nonequivalence of P₂ and P₄ is caused by ion association. In a recent publication we described the preparation of a platinum(II) hydride from picric acid and suggested that one of the PPh₃ groups was associated with the picrate.²¹ We have now found that the ¹H nmr of this complex corresponds to that with the trifluoroacetic acid compound, and the structures are therefore analogous.

The low-temperature nmr of the hydride resonance of the compound from CF₃COOH has been obtained down to -60°. The positions and widths of the resonances remain unchanged, and no new peaks appear. However, there is some broadening of the spectrum which is probably due to an increase in the viscosity of the solution. On warming back to room temperature, the spectrum reverts to its original form, but these low-temperature data give no positive evidence for any exchange occurring in solution. In addition there is no evidence for the formation of a platinum(IV) dihydride even when excess of the carboxylic acid is used. The integration of the hydride resonance corresponds very closely to a monohydride, and no other

peaks can be found in the spectrum. Since the nmr in pure CF₃COOH is the same as that in other solvents, it appears that even in this medium the second oxidative addition to the platinum(IV) dihydride does not occur. This does not mean that such a compound cannot be a reactive intermediate in the reactions forming (PPh₃)₂PtHX or (PPh₃)₂PtX₂ but suggests that if the mechanism involves a platinum(IV) dihydride, it is probable that it exists in low concentration as a transient species.

In an earlier study on complexes of the type [(PPh₃)₃-PtH]X,⁷ it was reported that the rather low conductivity could be explained by an equilibrium of the type



We have scanned the ¹H nmr spectrum of [(PPh₃)₃-PtH](CF₃COO)₂H up to higher field and find no evidence for a resonance at τ 31.3 which is the position for (PPh₃)₂Pt(H)COOF₃.² This indicates that if the bis complex is present in solution, its concentration must be quite small. The molecular weights for the trifluoroacetate, pentafluoropropionate, and chlorodifluoroacetate complexes have been obtained by osmometer and show a value in each case which is very close to the theoretical formula weight. This result would be in agreement with a coordinated carboxylate but could also be indicative of an ionic compound which was little dissociated in solution. It is not easy to differentiate between these options, but these data suggest that ion association could be an alternate explanation for the low conductivity of the complexes.

The addition of triphenylphosphine to a solution of these complexes in nitrobenzene causes the conductivity to increase,⁷ and we have found a similar behavior with the trifluoroacetate complex. This has been explained by assuming that a displacement of the above equilibrium occurs in favor of formation of the ionic compound. If the reaction is followed by observing the ¹H nmr spectrum, it is apparent that exchange occurs since the eight-line spectrum shown in Figure 2 collapses to two sharp singlets, which is the spectrum obtained from a mixture of (PPh₃)₄Pt and CH₃COOH. This rapid exchange appears to affect only the cis PPh₃ groups since the coupling of the trans PPh₃ groups with the hydride is only slightly affected. The value is reduced from 164 to 160 Hz, which is that found in the ¹⁹⁵Pt portion of the spectrum of the pure complex. The observed lability in the presence of excess phosphine has been previously reported in a similar system.²² The mechanism is probably phosphine exchange rather than an oxidative addition-reductive elimination one involving the hydride, since the H-Pt coupling constant of 774 Hz remains unchanged when PPh₃ is added. When PPh₂Me or PPhMe₂ is added, the ¹H nmr is different since now the center lines collapse to a singlet indicative of a rapid exchange of both cis and trans phosphines. This onset of rapid exchange is not promoted by the addition of other π -acid ligands such as carbon monoxide or ethylene to a solution of [(PPh₃)₃PtH](CF₃COO)₂H, and the addition of pyridine gives (PPh₃)₂Pt(H)-OOCF₃. In addition, we have found that the hydride does not exchange with D₂ gas, and under ambient

(20) The data which we have had to estimate are the differences in chemical shift between P₂, P₃, and P₄, as well as the P₂-P₃, P₃-P₄, and P₂-P₄ coupling constants. In the AB₂MX case it has also been necessary to estimate the P-Pt coupling constants.

(21) P. B. Tripathy and D. M. Roundhill, *J. Organometal. Chem.*, **24**, 247 (1970).

(22) P.-C. Kong and D. M. Roundhill, *Inorg. Chem.*, **11**, 749 (1972).

conditions the ^1H nmr spectrum indicates no insertion of 1,4-butadiene or hexafluorobutene-2.

In view of ion association being a feasible alternative explanation for the low conductivity of these complexes, we have studied the conductivity in more detail. We have found, in agreement with previous work,⁷ that the conductivity increases when triphenylphosphine is added to the solution, but it appears that a limiting value is reached when 1 mol of PPh_3 /mol of complex has been added. These results are shown in Table I

TABLE I
CONDUCTIVITY DATA ON $[(\text{PPh}_3)_3\text{PtH}](\text{CF}_3\text{COO})_2\text{H}$

Complex: PPh_3 mole ratio	Conduc- tivity, ohm^{-1} cm^2 equiv $^{-1}$	Complex: PPh_3 mole ratio	Conduc- tivity, ohm^{-1} cm^2 equiv $^{-1}$	Complex: PPh_3 mole ratio	Conduc- tivity, ohm^{-1} cm^2 equiv $^{-1}$
Pure complex	22.4	1.33	27.9	0.8	28.6
4.0	24.6	1.0	28.3	0.67	28.0
2.0	26.5				

but are not plotted graphically because of the errors incurred by the use of small amounts of PPh_3 . The limiting value of the conductivity is *ca.* $28 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$, which is very close to the result we have obtained for $[(\text{PPh}_3)_3\text{PtH}]\text{BPh}_4$ ($25.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$) and NaBPh_4 ($27.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$). This result suggests that the PPh_3 may cause dissociation of the ion pairs and lead to the formation of the coordinately saturated $(\text{PPh}_3)_4\text{PtH}^+$ ion. We have been unable, however, to isolate such a species since $[(\text{PPh}_3)_3\text{PtH}](\text{CF}_3\text{COO})_2\text{H}$ can be recrystallized unchanged even from a solution containing up to a 10 molar excess of PPh_3 .²³

Recently it has been found that two molecules of HCN will add to $(\text{PPh}_3)_3\text{RhCl}$, and a structure is proposed in which one molecule has oxidatively added to the Rh(I) complex and the other is coordinated as an undissociated molecule.²⁴ Such a structure would be possible with these platinum complexes, where the

(23) Since the complex containing a dimeric anion can be recovered in good yield from a large excess of PPh_3 , it is unlikely that the conductivity change simply involves one molecule of PPh_3 being protonated by the carboxylic acid.

(24) H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 2516 (1968).

trifluoroacetate is a monomeric anion and the other molecule is present as the free acid. When the single-crystal X-ray data are available, the location of this second molecule of acid will be exactly known; however, the assumption of a strongly bonded dimer similar to that in $\text{M}(\text{CF}_3\text{COO})_2\text{H}$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$)²⁵ has been made from the following information. A related study on the protonation of some Rh(I) and Ir(I) complexes with CF_3COOH has led to the isolation of $[(\text{MeOPPh}_2)_4\text{RhHCl}](\text{CF}_3\text{COO})_2\text{H}$ and $[(\text{PPh}_3)_3\text{Ir}(\text{CO})\text{H}_2](\text{CF}_3\text{COO})_2\text{H}$.²⁶ The ir spectra of these complexes in the carboxylate region are identical with that of $[(\text{PPh}_3)_3\text{PtH}](\text{CF}_3\text{COO})_2\text{H}$, and since these complexes contain a six-coordinate cation, it is very unlikely that this molecule of acid is directly bonded to the metal since this would lead to heptacoordination. If the molecule of acid were firmly coordinated, it would be probable that it would remain bonded even after displacement of the CF_3COO^- ion; however, the addition of NaBPh_4 to a solution of the complex leads to the formation of $[(\text{PPh}_3)_3\text{PtH}]\text{BPh}_4$ which is free from CF_3COOH . An alternate explanation is that the stoichiometry is due to a molecule of acid occluded in the lattice, but if this is correct, it is surprising that analytically pure samples can be obtained after five recrystallizations in the absence of CF_3COOH and after isolation from a tenfold excess of PPh_3 .

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(26) P.-C. Kong and D. M. Roundhill, *Inorg. Chem.*, **11**, 1437 (1972).