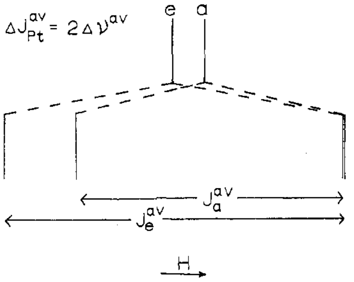

Figure 2.—Schematic explanation for the difference in satellite peak line widths in the particular case that the difference in coupling constants is exactly twice the chemical shift difference.

to a narrow satellite peak at high field and a broad satellite peak at low field.

Were conformational averaging complete and the chemical shift difference due solely to the inherent magnetic nonequivalence of the tris complex, a substantial difference in coupling constants to platinum would not be expected. If each ligand populated the δ and λ conformations equally, then each proton would possess an identical geometric relationship with the platinum. In this model a chemical shift difference arises from the magnetic effects of the other two chelate rings in the complex, not from their effects on the geometry of the ligand. The distribution of the ligands about the platinum is not expected to influence the scalar coupling through the Pt–N–C–H bonds. Neither is through-space dipole–dipole coupling expected. Dipole–dipole coupling is averaged to zero by rapid tumbling in solution except when the nuclei are in an anisotropic environment. The metal ion in a tris-diamine octahedral complex is nearly isotropic as indicated by the absence of effective nuclear quadrupole relaxation in $Co(en)_3^{3+}$.[16] The observed difference in coupling constants is therefore more likely the consequence of incomplete conformational averaging than the result of the asymmetry of the complex.

To determine the extent of conformational averaging, one additional assumption is necessary. Either the intrinsic chemical shift difference between an axial and an equatorial proton in a fixed conformation or the intrinsic coupling constants between platinum and the axial and equatorial protons in a single conformation are required. We chose to assume that the chemical shift difference between the axial and equatorial methylene protons observed in tris(propylenediamine)platinum(IV) ion[10] is appropriate for a single conformation of ethylenediamine. Using the value of $\Delta\nu^0$ of 13 ± 2 Hz for the intrinsic chemical shift difference,[10] the averaged chemical shift difference of 4 ± 1 Hz implies that 65 ± 5% of the ethylenediamine ligands are in the more stable conformation and 35 ∓ 5% in the less stable conformation.

The intrinsic platinum–proton coupling constant can now be calculated from this result together with the observed difference in the averaged coupling constants (ΔJ_{Pt}^{av} = 6 ± 1 Hz) and the sum of the averaged coupling constants (54 Hz, determined from the separation of the satellite peaks). The platinum–equatorial proton coupling constant is calculated to be 40 ± 5 Hz, and the platinum–axial proton coupling constant, 15 ∓ 5 Hz. These values are in accord with other observations[15] that the equatorial proton is more strongly coupled to the metal ion than is the axial proton and thus support the assumptions made in evaluating them.

We conclude that conformational preferences exist for the ethylenediamine ligands in $Pt(en)_3^{4+}$ in solution since complete conformational averaging does not account for the differences in platinum–proton coupling constants. Since incomplete conformational averaging of the coupling constants is needed to explain the asymmetry of the satellite peaks, this effect must also be included in explaining the chemical shift difference. Assuming only incomplete conformational averaging effects, the spectra can be fit and reasonable values of the ^{195}Pt coupling constants calculated; hence the inherent magnetic nonequivalence of an ethylenediamine ligand in a tris complex must not contribute significantly to the observed chemical shift difference.

The extent of conformational averaging is comparable to that found for $Ru(en)_3^{2+}$ [10] and $Ni(en)_3^{2+}$,[1] which suggests that the charge on the complex does not substantially alter the conformational energies. The relatively narrow lines of the $Pt(en)_3^{4+}$ spectra compared with those of $Ru(en)_3^{2+}$ and $Rh(en)_3^{3+}$ are better explained[9,10] in terms of the relatively small intrinsic chemical shift difference between the axial and equatorial protons, probably a consequence of the high oxidation state of the metal.

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Preparation of Salts of the Bis(triphenylphosphine oxide)hydrogen(I) Cation

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Collamati[1] has reported the reformulation of the compound $HAuCl_4 \cdot 2(C_6H_5)_3PO$ as $\{[(C_6H_5)_3PO]_2H\}AuCl_4$. Potts[2] has recently extended the work to include other protonic complexes of oxo ligands with $HAuCl_4$. During studies of the chemistry of triphenylphosphine oxide with several metal salts, additional examples of

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this type of behavior were observed. We wish to report the results of these findings, along with the investigation of the hydrogen chloride and hydrogen perchlorate compounds.

Experimental Section

Materials.—The triphenylphosphine oxide was obtained from M and T Chemicals, Inc., and used as received. Rhenium(V) chloride was prepared by a modification of the method of Hurd and Brimm[3] and β-rhenium(IV) chloride was obtained from Shattuck Chemical Co. Indium perchlorate octahydrate was obtained from Alfa Inorganics. Baker and Adamson 70% perchloric acid was used as received, while hydrogen chloride was generated by the action of sulfuric acid on sodium chloride.

Analyses.—The carbon and hydrogen analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The chloride content was determined by the gravimetric method of Beamish.[4]

Physical Measurements.—Infrared spectra were obtained as Nujol mulls or KBr pellets on a Perkin-Elmer 521 spectrophotometer. Visible spectra were obtained on a Beckman DK-2A spectrophotometer in methylene chloride.

Preparation of the Compounds. **$\{[(C_6H_5)_3PO]_2H\}_2Re_2Cl_9$.**—Rhenium(V) chloride, 0.66 g (1.8 mmol), was dissolved in 25 ml of acetone giving a dark green solution. To this was added triphenylphosphine oxide, 2.38 g (8.4 mmol), in 15 ml of acetone. The solution was allowed to stand capped in a drybox, and after 2 days the solution contained dark violet crystals. The product was isolated by filtration, washed with acetone, and dried to give 0.72 g (76.5%) of product. It was recrystallized from acetone–ether. *Anal.* Calcd for $C_{72}H_{62}O_4P_4Re_2Cl_9$: C, 47.87; H, 3.46; Cl, 17.66. Found: C, 48.14; H, 3.62; Cl, 16.93. The molar conductivity determined in acetonitrile was 258 ohm^{-1} cm^2. The visible spectrum was the same as that obtained previously for the $Re_2Cl_9^{2-}$ ion.[5]

The same compound was made in an analogous fashion from β-$ReCl_4$. This conclusion was based on elemental analyses and infrared and visible spectra. In both cases, the anion was reduced to the $Re_2Cl_8^{2-}$ ion upon standing in acetone.

$\{[(C_6H_5)_3PO]_2H\}ClO_4$.—To a solution of 1.50 g (5.4 mmol) of triphenylphosphine oxide in 10 ml of ethanol was added 0.54 g (3.8 mmol) of 70% $HClO_4$. After standing for 8 hr, the solution was concentrated to half the initial volume. Upon cooling, white crystals of $\{[(C_6H_5)_3PO]_2H\}ClO_4$ were obtained. The product was isolated by filtration, washed with ethanol, and dried to yield 0.30 g (16.9%) of product. It was recrystallized from ethanol. No attempt was made to maximize the yield. *Anal.* Calcd for $C_{36}H_{31}P_2O_6Cl$: C, 65.81; H, 4.76. Found: C, 65.38; H, 4.75.

$(C_6H_5)_3PO \cdot HCl$.—Hydrogen chloride was bubbled through a solution of 2.0 g (7.2 mmol) of triphenylphosphine oxide dissolved in 25 ml of ethanol for 2 hr. The solution was allowed to evaporate slowly until crystals formed. The solid was isolated by filtration, washed with diethyl ether, and dried. The white solid weighed 0.75 g (33.2%). No attempt was made to increase the yield. *Anal.* Calcd for $C_{18}H_{16}POCl$: C, 68.69; H, 5.12. Found: C, 67.96; H, 5.37. The melting point is 112–114°, which is in agreement with that obtained by Hadzi.[6]

Results and Discussion

Recently it was shown that rhenium(V) chloride and water react as follows[7]

$$7ReCl_5 + 12H_2O \longrightarrow 2Re_2Cl_9^{2-} + 3ReO_4^- + 17HCl + 7H^+$$

The water serves as an agent for the dimerization of the rhenium and for the formation of an acid solution necessary for the formation of the cation $[(C_6H_5)_3PO]_2H^+$. In the present work, water can come from two sources. It may be an impurity in the acetone or may be produced from the condensation of acetone, which has been shown to occur in the presence of rhenium(V) chloride.[8] Since no other solvents have been found in which rhenium(V) chloride and triphenylphosphine oxide react, this reaction again illustrates the unique character of acetone. Rhenium(V) chloride was shown to react differently from $MoCl_5$, $TaCl_5$, or $NbCl_5$, where oxygen abstraction from the triphenylphosphine oxide takes place.[9]

During a study of the coordination chemistry of indium, a second compound containing the cation was observed. When solid $In(ClO_4)_3 \cdot 8H_2O$ was exposed to moist air, it turned to a semiliquid. The reaction of this material with triphenylphosphine oxide in ethanol did not lead to the desired product $\{In[(C_6H_5)_3PO]_4\}(ClO_4)_3$[10] but to $\{[(C_6H_5)_3PO]_2H\}ClO_4$. It is felt that, upon standing, the $In(ClO_4)_3 \cdot 8H_2O$ reacts further with water to form perchloric acid and some unknown indium species, with the subsequent reaction of perchloric acid with triphenylphosphine oxide. This was shown to be the case, since the utilization of new, solid $In(ClO_4)_3 \cdot 8H_2O$ led to the isolation of the anticipated indium complex, while the reaction of perchloric acid and triphenylphosphine oxide resulted in the isolation of $\{[(C_6H_5)_3PO]_2H\}ClO_4$.

As Hadzi[6] had reported formation of $\{[(C_6H_5)_3PO]_2H\}Cl$ and its infrared spectrum, we attempted to reproduce it for comparison of the infrared spectrum to the compounds described in this paper. Numerous attempts to produce the complex were unsuccessful. These included varying the mole ratio of hydrogen chloride to triphenylphosphine oxide, as well as the amount of water present in the ethanol. Only $(C_6H_5)_3PO \cdot HCl$ was isolated, and its infrared spectrum and elemental analyses were invariant after 1 year. We are unable to account for this difference.

The infrared spectra of the salts are indicative of a hydrogen-bonded cation with a broad band in the area of 1000–800 cm^{-1}. In the hydrogen-bonding region, these spectra compare favorably with those obtained for $[(antipyrine)_2H]ClO_4$[11] and the protonic complexes of $HAuCl_4$.[2] The spectrum of $(C_6H_5)_3PO \cdot HCl$ is identical with that obtained by Hadzi for $\{[(C_6H_5)_3PO]_2H\}Cl$. In the case of the perchlorate salt the presence of noncoordinated ClO_4^- is indicated. The features are otherwise routine.

We believe that these results indicate that the formation of the cation is more widespread than previously thought, and its existence should be possible in an acid solution which contains a bulky noncoordinating anion.

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The Reaction of Hydrogen Cyanide with Bis[1,4-bis(diphenylphosphino)butane]nickel(0)

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Recently it has been reported that the Ni(0) complexes $Ni(P(OC_2H_5)_3)_4$ and $Ni(P(C_6H_5)_2(CH_2)_2P$-