

Figure 2. The (110), (202), and (004) powder neutron diffraction peaks of CsAuCl_3 at 1 and 28 kbar.

temperature conductivity of $10^{-6} \Omega^{-1} \text{cm}^{-1}$ at ambient pressure up to $10^{-1} \Omega^{-1} \text{cm}^{-1}$ at 28 kbar. Because the two Au sites in the unit cell must still remain crystallographically inequivalent at 28 kbar, this very large increase must be due to a lowering of the activation energy in a semiconducting phase rather than the transformation of the semiconducting phase into a metallic phase. In other words at 28 kbar CsAuCl_3 is still a class II mixed-valence salt.

A final point of interest concerns the compressibility of the salt. Defining the linear axial compressibility as the compressive strain per unit pressure $-(1/l)(dl/dP)$, where $l = a$ and c , we calculate values of 0.95×10^{-2} and $1.03 \times 10^{-2} \text{cm}^2 \text{dyn}^{-1}$ along the a and c axis, respectively. These are to be compared with values⁹ for simple ionic salts such as NaCl ($1.42 \times 10^{-2} \text{cm}^2 \text{dyn}^{-1}$) and CsCl ($1.98 \times 10^{-12} \text{cm}^2 \text{dyn}^{-1}$) and indicate that despite the very large increase in conductivity brought about by pressure, the elastic properties of CsAuCl_3 are not notably unusual. We hope to extend our measurements to higher pressures using a newly constructed¹⁰ sapphire cell.

After the experiments described here were completed, we became aware of a parallel investigation of the high-pressure structure of CsAuCl_3 by X-ray diffraction.¹¹ We are grateful to Professor Dr. H. Schulz and Dr. W. Denner for communicating these results to us and helping to index the 26–27° region of our scans.

Registry No. CsAuCl_3 , 54586-01-5.

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A Five-Coordinate Palladium(II) Complex Containing Tris(2-(dimethylamino)ethyl)amine, $\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$

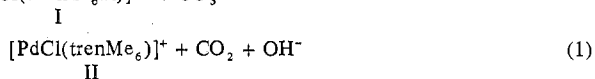
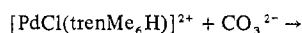
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Although five-coordinate complexes of the type $[\text{M}(\text{trenMe}_6)\text{X}]\text{X}$ (M = a first-row transition metal; $\text{trenMe}_6 = \text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_3$; X = an anionic ligand) are known,¹⁻⁴ analogous five-coordinate derivatives containing a second- or third-row transition metal have not yet been reported.

Results and Discussion

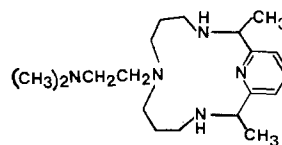
The molecular structure of the four-coordinate cation $[\text{PdCl}(\text{trenMe}_6\text{H})]^{2+}$ isolated as $[\text{PdCl}(\text{trenMe}_6\text{H})]\text{ClPF}_6$ has been determined.⁵ We now report that when the foregoing cation is formed in situ in aqueous solution and the pH of the solution is adjusted to about 11.5 with Na_2CO_3 , the protonated N,N -dimethylaminoethyl portion of the coordinated ligand is neutralized and coordinates to the palladium center according to eq 1. The product, II, may be readily isolated as the



chloride salt, $[\text{PdCl}(\text{trenMe}_6)]\text{Cl}$ (see Experimental Section).

At $\text{pH} \leq 7.0$, $[\text{PdCl}(\text{trenMe}_6\text{H})]^{2+}$ is present in solution and may be isolated as the chloride salt $[\text{PdCl}(\text{trenMe}_6\text{H})]\text{Cl}_2$. The proton NMR spectrum of I in D_2O exhibits a doublet (3.27 and 3.17 ppm) and a singlet (2.70 ppm) in a ratio of 2:1 downfield from DSS and is shown in Figure 1. The doublet resonance may be attributed to the magnetically nonequivalent methyl hydrogens of the N,N -dimethylaminoethyl groups bonded to palladium and the singlet may be attributed to the methyl groups of the protonated N,N -dimethylaminoethyl group. At $\text{pH} \sim 12$, II is present in solution and its proton NMR spectrum is characterized by a sharp, singlet methyl resonance (2.6 ppm) in D_2O .

The proton NMR spectrum shown in Figure 1 is consistent with the presence of six magnetically equivalent methyl groups, i.e., the ligand is acting as a tetradentate ligand. The geometry about the palladium is presumably trigonal bipyramidal, similar to that observed for other five-coordinate complexes containing trenMe_6 .⁶ The chloride salt of II behaves as a 1:1 electrolyte in aqueous solution (see Experimental Section). These data together with the analytical data presented in Table I are consistent with the formation of a five-coordinate palladium(II) complex according to eq 1. Recently, a pH-induced geometrical change similar to that described herein has been reported for the macrocyclic ligand III coordinated to nick-



III

Table I. Analytical Data

compd	% C		% H		% N		% Cl	
	calcd	found	calcd	found	calcd	found	calcd	found
[PdCl(trenMe ₆ H)]Cl ₂	32.67	33.05	7.03	7.65	12.71	12.51	23.45	23.22
[PdCl(trenMe ₆)Cl]	35.53	34.95	7.40	7.45	13.82	13.37	17.00	17.24
[PdCl(trenMe ₆ H)](ClO ₄) ₂	25.32	24.98	5.45	5.51	9.85	9.60	18.17	18.27
[PdCl(trenMe ₆ H)](BF ₄) ₂	26.40	25.89	5.68	5.92	10.27	10.06	6.32	6.53

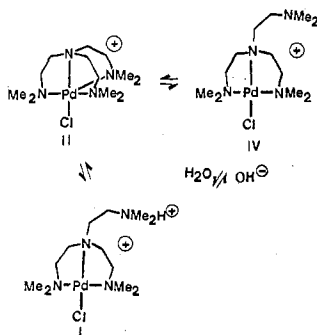
el(II).⁷ At low pH (<6.3) the complex is square planar with a protonated exocyclic *N,N*-dimethylaminoethyl group. At pH > 7 the *N,N*-dimethylaminoethyl group coordinates to the nickel center to form a five-coordinate complex.

In the presence of anions such as perchlorate and tetrafluoroborate the salts [PdCl(trenMe₆H)]X₂ (X⁻ = ClO₄⁻, BF₄⁻) are readily precipitated from aqueous solutions of II. These complexes have been characterized by their elemental analyses and proton NMR spectra as well as their infrared spectra which exhibit absorption bands characteristic of the ligand and the uncoordinated counterion. It may, therefore, be concluded that equilibrium 2 is present in aqueous solution

$$[\text{PdCl}(\text{trenMe}_6)]^+ + \text{H}_2\text{O} \rightleftharpoons [\text{PdCl}(\text{trenMe}_6\text{H})]^{2+} + \text{OH}^- \quad (2)$$

and that the equilibrium is shifted in favor of the four-coordinate complex as a consequence of the low solubility of the perchlorate and tetrafluoroborate salts.

However, it must be noted that the proton NMR spectrum of II does not preclude the presence of a rapid equilibrium (on the NMR time scale) between the five-coordinate cation and a four-coordinate species having one uncoordinated *N,N*-dimethylaminoethyl group. Since this latter species, IV, can be readily protonated in aqueous solution to yield I, the proton NMR spectrum of II also does not preclude the presence of a rapid equilibrium (on the NMR time scale) between IV and I. It therefore follows that the equilibrium shown in eq 2 should also be rapid on the NMR time scale. These equilibria are schematically shown below.



Complex II represents the first reported example of a five-coordinate complex of a second-row transition metal coordinated to the tripod ligand trenMe₆. Further aspects of the chemistry of this and related derivatives are under investigation.

Experimental Section

Proton NMR spectra were recorded on a Varian A60 or T60 spectrometer. The internal reference for D₂O solutions was 2,2-dimethyl-2-silapentane-5-sulfonate, DSS, and tetramethylsilane, Me₄Si, for other solvents. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls or KBr disks. Electrical conductivity measurements were made using a Beckman Model RC-18H conductivity bridge. Microanalyses were performed by MHW Laboratories, Garden City, Mich.

Materials. Palladium(II) chloride was purchased from Johnson Matthey and Mallory Ltd. The ligand tris(2-(dimethylamino)ethyl)amine was prepared according to the literature method.¹ All other chemicals used were reagent grade.

Chloro[bis(2-(dimethylamino)ethyl)](2-(dimethylaminium)ethyl)amine]palladium(2+) Chloride, [PdCl(trenMe₆H)]Cl₂. Palladium(II)

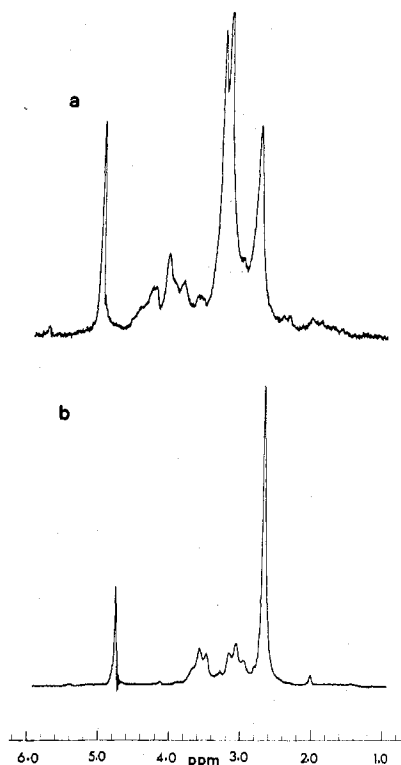


Figure 1. Proton NMR spectra of (a) [PdCl(trenMe₆H)]Cl₂ in D₂O and of (b) [PdCl(trenMe₆)]Cl in D₂O.

chloride (1.0 g, 5.6 mmol) and 1.0 mL of concentrated hydrochloric acid were added to about 40 mL of water, and the mixture was heated under reflux until all the palladium chloride dissolved. The solution was then cooled to room temperature and trenMe₆ (1.65 g, 8.5 mmol) was slowly added. The solution was then refluxed for a further 30 min. After the solution was cooled to room temperature, small portions of Na₂CO₃ were added until the pH of the solution was raised to about 7 ("colorpHast" indicator stick). The solvent was then removed by means of a roto-evaporator. The remaining residue was dissolved in about 50 mL of ethanol, and NaCl was filtered off. This procedure was repeated several times until all the NaCl was separated from the solution. The crude product was recrystallized from hot ethanol, collected by filtration, washed with acetone, and dried in vacuo over boiling ethanol.

Chloro[tris(2-(dimethylamino)ethyl)amine]palladium(1+) Chloride, [PdCl(trenMe₆)]Cl. An aqueous solution of [PdCl(trenMe₆H)]²⁺ was prepared as above. An excess of Na₂CO₃ was then added to the solution to bring the pH to about 11.5 ("colorpHast" indicator stick). The reaction was then worked up as before via repeated extraction-filtration-evaporation cycles with ethanol to completely remove NaCl and any unreacted Na₂CO₃. The product was finally washed with a small amount of acetone and dried in vacuo over boiling ethanol. The complex is hygroscopic. Its molar conductivity was observed to be 143 Ω⁻¹ cm² mol⁻¹ (concentration ≈ 10⁻³ M) at 25 °C.

Chloro[bis(2-(dimethylamino)ethyl)](2-(dimethylaminium)ethyl)amine]palladium(2+) Tetrafluoroborate, [PdCl(trenMe₆H)](BF₄)₂. An aqueous solution of [PdCl(trenMe₆)]Cl (0.50 g in 10 mL) was prepared, and to this was added an excess of NaBF₄ via a filtered, saturated solution (10–15 mL). The precipitate which formed was collected, washed with cold methanol and then acetone, and dried in vacuo at room temperature. The crude complex was recrystallized from hot water as fine needles. The proton NMR spectrum in CD₃CN

showed a broad singlet at 2.95 ppm (2 protons) and a singlet at 2.65 ppm (1 proton).

Chloro[bis(2-(dimethylamino)ethyl)][2-(dimethylaminium)ethylamine]palladium(2+) Perchlorate, [PdCl(trenMe₆H)](ClO₄)₂. This complex was prepared and purified in an analogous manner to that used for the tetrafluoroborate analogue. The limited solubility of the perchlorate derivative precluded the recording of its proton NMR spectrum.

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Registry No. [PdCl(trenMe₆H)]Cl₂, 66632-98-2; [PdCl(trenMe₆H)]Cl, 66632-97-1; [PdCl(trenMe₆H)](ClO₄)₂, 66632-96-0; [PdCl(trenMe₆H)](BF₄)₂, 66632-94-8.

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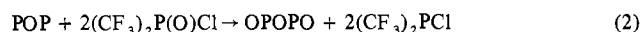
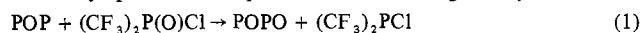
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Bis(trifluoromethyl)phosphoryl-μ-oxo-bis(trifluoromethyl)-phosphine. The Mixed Anhydride of a Phosphinous and Phosphinic Acid

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In a review publication some years ago,¹ it was implied that the unknown compound (CF₃)₂POP(O)(CF₃)₂ (hereinafter written as "POPO") would be stable against disproportionation into (CF₃)₂POP(CF₃)₂ and [(CF₃)₂PO]₂O (hereinafter, "POP" and "OPOPO"). The basis of this prediction was the ROQ rule: if R and Q differ enough in regard to π-acceptor bonding strength, ROQ will be formed irreversibly from ROR and QOQ. In fact, POPO now has been made by the following virtually quantitative processes, occurring easily at 25 °C.



These processes represent an extension of an earlier series of quantitative reactions whereby (CF₃)₃P was NO₂ oxidized to (CF₃)₃PO, convertible to (CH₃)₂NP(O)(CF₃)₂ and finally to (CF₃)₂P(O)Cl.² Reaction 2 represents a new way to make OPOPO, but more direct is an improved procedure for NO oxidation of P₂(CF₃)₄,³ attack by NO upon the slowly warming liquid leads to a high yield of pure OPOPO. In contrast, P₂(CF₃)₄ vapor (50 °C) is converted by NO to pure POPO in high yield. In reactions 1, 2, and 3, P₂(CF₃)₄ (an impurity in POP) remains inert.

Almost simultaneously with the prediction of a stable POPO came reports of the analogous F₂POP(O)F₂,⁴⁻⁶ F₂PSP(S)PF₂,⁶ and (CF₃)₂PSP(S)(CF₃)₂.⁶ In F₂POP(O)F₂ it was expected that F→P π bonding would weaken the O→P π bonding, making the ROQ rule less applicable. However, the decomposition of F₂POP(O)F₂ was complicated, making it difficult to demonstrate disproportionation, although F₂POP(F)₂ was one observed product.⁵

Table I. Relevant NMR Parameters^a

	¹⁹ F		³¹ P	
	δ	J _{FCP}	δ	J _{PCF}
POPO	65.6	93.1	-91.4	92.9
	72.5	131.9	+0.3	131.8
POP	66.5	"98.8" ^b	-99.3	Complex
OPOPO ^c	72.03	137.5	+5.4	137.5
P ₂ (CF ₃) ₄	47	"84.9" ^b	+9.0	Complex
(CF ₃) ₂ PCl	63.3	85.1	-50.2	85.0
(CF ₃) ₂ P(=O)Cl	72.3	129.8	-10.8	129.4

^a The chemical shifts, δ, are measured from Cl₃CF or H₃PO₄, with the upfield direction positive. ^b Second-order spectra; cf. ref 7. ^c Simple ¹⁹F doublet and ³¹P septet; no second-order pattern; cf. ref 3.

Experimental Methods

A modified Stock-type high-vacuum manifold (including mercury float-valves) was used for quantitative work with the volatile compounds here studied. For accurate ¹⁹F and ³¹P NMR spectra, the Varian XL-100-FT instrument was employed, with (CD₃)₂CO as the lock standard in 4.2 mm i.d. tubes and the samples in smaller sealed glass inserts. For rapid monitoring of a reaction, the ¹⁹F spectrum was observed by the Varian T-60 instrument.

Procedures and Results

Reaction 1. The reactants (0.339 mmol of POP and 0.321 mmol of the phosphinyl chloride) were condensed together in a 2.5 mm i.d. NMR tube insert, which then was sealed off from the vacuum line. The ¹⁹F spectrum (T-60), taken after 20 min at 25 °C, showed not only the (CF₃)₂P(O)Cl doublet and the known second-order pattern of POP⁷ but also the incipient presence of (CF₃)₂PCl. Two other doublets represented POPO; one was almost perfectly superposed upon the (CF₃)₂P(O)Cl doublet, but made it seem ragged. After 16 h at 25 °C, the POP spectrum had almost disappeared. The final spectrum, recorded by the XL-100-FT instrument after 11 days, showed the barely detectable excess of POP and full and equal intensity for the (CF₃)₂PCl and the two POPO doublets. The upfield POPO doublet now had replaced that for (CF₃)₂P(O)Cl, with a slightly different chemical shift and a distinctly different coupling constant. The pertinent NMR parameters are compared in Table I.

The ³¹P NMR spectrum of this final mixture showed the known (CF₃)₂PCl septet,⁸ between the two POPO septets, which differed in sharpness and saturability. Especially the downfield POPO septet showed tall, sharp peaks; P-O-P coupling was not detectable. In view of a simple septet for OPOPO, in contrast to a second-order spectrum for POP, it may be that the lack of P-O-P coupling in POPO relates to the bonding on the phosphorus(V) side. With the noise level at 0.5% of the highest peak, the spectrum failed to show either OPOPO or (CF₃)₂P(O)Cl.

Reaction 2. A mixture of 2.30 mmol of (CF₃)₂P(O)Cl and 1.00 mmol of POP, plus 0.025 mmol of P₂(CF₃)₄ impurity, was monitored by its ¹⁹F NMR spectrum (T-60 instrument), showing complete reaction after 18 h at 25 °C. The relative intensity of the small second-order P₂(CF₃)₄ spectrum⁷ remained unchanged. It now was possible to remove 2.10 mmol of (CF₃)₂PCl and 0.20 mmol of unused (CF₃)₂P(O)Cl and to isolate 0.96 mmol of virtually pure OPOPO, having the previously described properties.³ Since OPOPO condenses as clean white crystals melting near -42 °C, its vapor-pressure curve (log P vs. 1/T) is much steeper at lower temperatures, than that of P₂(CF₃)₄, POP, or other more volatile components, which are easily removed by slow passage through a U-trap in vacuo at -60 °C. The very clean NMR spectra of the final product (Table I) indicated its purity.

Reaction 3. The ¹⁹F NMR spectrum of a mixture of POP (0.428 mmol) and OPOPO (0.403 mmol) was observed at intervals, showing 18% conversion of POP to POPO after 20