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Tris(2-aminoethyl)amine Complexes of Palladium(II)

S. N. BHATTACHARYA† and CAESAR V. SENOFF*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ont. N1G 2W1, Canada

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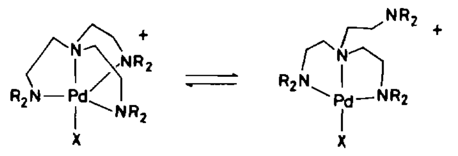
The syntheses of a series of complexes of the type, [PdX(tren)] Y where tren = $N(CH_2CH_2NH_2)_3$*, X = Cl,* BPh_4^- *are described and their physico-chemical pro-* BPh_4 *are described and their physico-chemical properties compared with the trenMe₆ analogues where trenMe₆ =* $N(CH_2CH_2N(CH_3)_2)_3$*. The available data suggest that these complexes are four coordinate in the solid state but exist in solution as an equilibrium involving five and four coordinate species. In the presence of* ClO_4^- *ion,* $[Pd(NCS)(tren)]^+$ *forms* $[Pd(NCS)(trenH)](ClO_4)_2$ *where trenH =* $N(CH_2CH_2NH_2)_2(CH_2CH_2NH_3^+)$*. The complex having X = NCS undergoes an N → S isomerization when the anion is changed from* SCN^- *to* BPh_4^-*.*

Introduction

Over 50 years ago Mann and Pope [1, 2] described the preparation of several palladium(II), platinum(II) and platinum(IV) complexes having tris(2-aminoethyl)amine, tren, as one of the ligands. Recent work from our laboratory has been concerned with aspects of the chemistry associated with related complexes of palladium(II) having tris(2-dimethylaminoethyl)amine, trenMe$_6$, as one of the ligands [3, 4, 5]. We have demonstrated that complexes of the type [PdX(trenMe$_6$)]X (X = Cl, Br, I, or SCN) exist in solution as an equilibrium involving four and five coordinate species as shown in eqn. (1) (R = CH_3)



(1)

even though these complexes are probably all four coordinate in the solid state since this has been shown to be the case for [Pd(NCS)(trenMe$_6$)]SCN [6].

We now wish to report the results of a comparative study which was undertaken with palladium(II) and tren as ligand in place of trenMe$_6$.

Results and Discussion

Attempts to generate $[PdCl(tren)]^+$ in solution *via* an initial reaction between $PdCl_4^{2-}$ and tren in acid solution followed by an adjustment of the pH failed. Considerable reduction to metallic palladium was observed together with the formation of $N(CH_2CH_2NH_3)_3Cl_3$, tren·3HCl. Instead, $PdCl_2$ was reacted directly with the ligand in aqueous solution for a prolonged period of time according to eqn. (2) to yield $[PdCl(tren)]^+$ in solution. The covalently bonded chloride could be readily replaced by Br^-, I^-, or SCN^- by

$$PdCl_2 + tren \xrightarrow[H_2O]{\Delta} [PdCl(tren)]Cl \qquad (2)$$

$$[PdCl(tren)]Cl + NaX \longrightarrow [PdX(tren)]X + NaCl \qquad (3)$$

metathesis in water according to eqn. (3). Analytical data for these diamagnetic complexes are given in Table I together with electrical conductivity data for the water soluble derivatives.

Unfortunately it was not possible to obtain nmr data for these complexes in solution because of their limited solubility. However, the tetraphenylborate salt of $[Pd(CNS)(tren)]^+$ [7] was prepared in an attempt to improve the solubility. This approach was reasonably successful and [Pd(CNS)tren)]BPh$_4$ was sufficiently soluble in acetonitrile to obtain a ^1H nmr spectrum. The NH_2 protons occur as a broad singlet at 2.80 ppm which disappeared after the addition of a small amount of D_2O to the solution because of exchange. This observation suggests that for the $[PdX(tren)]^+$ complexes an equilibrium similar to that shown in eqn. (1) (R = H) is present in solution and is occurring rapidly on the nmr time scale. This equilibrium was not investigated further as a function of temperature because of the limited solubility of the complexes in a suitable solvent.

The infrared spectrum of [Pd(CNS)(tren)]SCN is consistent with the presence of an N-bonded thiocyanato group which is also present in the trenMe$_6$ analogue, [Pd(NCS)(trenMe$_6$)]SCN [4]. Pertinent infrared spectral data are given in Table II.

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†On leave from Lucknow University, Lucknow, India.
*Author to whom correspondence should be addressed.

TABLE I. Analytical and Electrical Conductivity Data for [PdX(tren)] Y Complexes.

Complex		Calc				Found				Λ_M[a]
X	Y	%C	%H	%N	%X	%C	%H	%N	%X	
Cl	Cl	22.28	5.56	17.31	21.92	22.52	5.77	17.08	21.79	153
Br	Br	17.47	4.36	13.58	38.76	17.48	4.56	13.48	38.69	154
I	I	14.23	3.55	11.06		14.14	4.08	10.87		137
SCN	SCN	26.06	4.88	22.78	17.39[b]	25.15	4.76	21.46	15.64[b]	129
Br	ClO_4	16.68	4.16	12.96	8.20[c]	16.49	3.97	12.53	8.15[c]	
I	ClO_4	15.04	3.76	11.69	26.50[d]	15.16	3.70	11.74	26.31[c]	
SCN	BPh_4	59.13	6.03	11.11	5.09[b]	59.75	6.22	10.85	5.12[b]	
SCN[e]	ClO_4[e]	16.45	3.52	13.71		16.32	4.04	13.14		

[a] Recorded in water at 25 °C, concentration ~1×10^{-3} *M*. [b] %S. [c] %Cl. [d] %I. [e] $[Pd(NCS)(trenH)](ClO_4)_2$.

TABLE II. Infrared Spectral Data.

Complex	ν(CN) (cm^{-1})	ν(CS) (cm^{-1})
[Pd(NCS)(tren)] SCN	2066s 2048s[a]	770w 753w[a]
$[Pd(SCN)(tren)]BPh_4$	2113s	[b]
$[Pd(NCS)(trenH)](ClO_4)_2$	2050s	[b]

[a] Ionic SCN^-. [b] Masked by anion absorptions, s = strong, w = weak.

It may also be noted from the data given in Table II that in changing the counter ion from SCN^- to BPh_4^-, there is a pronounced increase in the ν(CN) frequency which is reminiscent of the anion dependent isomerization reported for Pd(II) derivatives of Et_4dien and $MeEt_4$dien [8, 9]. Although the available data cannot unequivocally confirm or discount that a similar isomerization has occurred for the tren complexes reported herein, the large increase in the ν(CN) frequency in changing the counter ion from SCN^- to BPh_4^- would seem to suggest that an N→S isomerization has occurred.

It was previously noted that the $[PdX(trenMe_6)]^+$ complexes were readily protonated in aqueous solution to form $[PdX(trenMe_6H)]^{2+}$ [3, 4]. There apparently is less tendency for the tren analogues to behave in a similar fashion since only $[Pd(NCS)(tren)]^+$ was protonated in water under similar experimental conditions used to isolate the protonated $trenMe_6$ complexes. In most cases a simple anion exchange was observed (see experimental section). The precise reason for this difference in behaviour between tren and $trenMe_6$ is not readily apparent but is undoubtedly due in part to the more basic NMe_2 group which is present in $trenMe_6$.

In summary, the available data indicate that the coordinating properties of tren are very similar to those of $trenMe_6$ towards Pd(II) and that complexes of the type $[PdX(trenMe_6)]^+$ and $[PdX(tren)]^+$ both occur in solution as an equilibrium between a four and a five coordinate species as shown in eqn. (1) when R = CH_3 or H. Also, in view of the fact that the $trenMe_6$ complexes are four coordinate in the solid state, it would seem reasonable to conclude that the tren complexes are four coordinate in the solid state as well.

Experimental

Palladium(II) chloride was obtained from Johnson-Mathey & Mallory Ltd. and tris(2-aminoethyl)amine from the Ames Laboratories, Inc. Other chemicals used were reagent grade or better.

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls or KBr discs. ^1H nmr spectra were recorded on a Varian A60 or a Bruker WP60 spectrometer. Microanalyses were carried out by M.H.W. Laboratories, Phoenix Arizona and Guelph Chemicals Ltd., Guelph.

Chloro Tris(2-aminoethyl)aminepalladium(II) Chloride, [PdCl(tren)] Cl

To a suspension of $PdCl_2$ (1.00 g, 5.64 mmol) in water (30 ml) at room temperature was added tris(2-aminoethyl)amine (0.82 g, 5.64 mmol) in a dropwise fashion and the resulting mixture was stirred for about 12 h during which time the color of the suspension changed from brown red and a greenish brown solution formed accompanied by the deposition of a small amount of metallic palladium. The solution was filtered by gravity and the filtrate heated on a water bath for about 3 h. The solvent was then carefully removed under vacuum with the aid of a roto-evaporator and the product isolated as a light yellow solid which was washed in succession with a small amount of cold water, absolute ethanol and finally dried *in vacuo* at room temperature.

Bromo Tris(2-aminoethyl)aminepalladium(II) Bromide, [PdBr(tren)]Br

To a warm solution of [PdCl(tren)]Cl (0.64 g, 1.9 mmol) in water (25 ml) was added a concentrated solution of NaBr (0.61 g, 6.0 mmol) in water (7 ml). The resulting solution was then stirred at room temperature for 24 h during which time a light yellow precipitate formed. The precipitated product was collected by filtration, washed in succession with cold water, absolute ethanol and dried *in vacuo* at room temperature.

Thiocyanato-N-tris(2-aminoethyl)aminepalladium(II) Thiocyanate, [Pd(NCS)(tren)]SCN

This complex was prepared in a similar manner used to prepare [PdBr(tren)]Br but NaSCN was used in place of NaBr.

Iodo Tris(2-aminoethyl)aminepalladium(II) Iodide, [PdI(tren)]I

This complex was prepared by reaction of [PdCl(tren)]Cl with NaI in aqueous solution as described above for [PdBr(tren)]Br. The reaction was rapid and the product precipitated from solution almost immediately.

Bromo Tris(2-aminoethyl)aminepalladium(II) Perchlorate, [PdBr(tren)]ClO_4

To a warm solution of [PdBr(tren)]Br (0.50 g, 0.98 mmol) in water (25 ml) was slowly added a solution of $NaClO_4$ (0.12 g, 1.0 mmol) in water (5 ml). The product immediately precipitated from solution and was collected by filtration, washed in succession with water, ethanol and finally dried *in vacuo* over $CaCl_2$.

Iodo Tris(2-aminoethyl)aminepalladium(II) Perchlorate, [PdI(tren)]ClO_4

This complex was prepared in a similar manner used for [PdI(tren)]ClO_4 but starting with [PdI(tren)I].

Thiocyanato-S-tris(2-aminoethyl)aminepalladium(II) tetraphenylborate, [Pd(SCN)(tren)]BPh_4

To a stirred, warm aqueous solution of [Pd(NCS)(tren)]SCN (0.36 g, 0.97 mmol) in water (20 ml) was added a concentrated solution of $NaBPh_4$. The cream colored precipitate was collected by filtration, washed in succession with water, ethanol and finally dried *in vacuo* at room temperature.

Thiocyanato-N-[bis(2-aminoethyl)] [2-ammonioethyl]aminepalladium(II), [Pd(NCS)(trenH)]$(ClO_4)_2$

This complex was prepared in a manner similar to that used for the other perchlorate salts described above but starting with [Pd(NCS)(tren)]SCN.

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