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Palladium(II) Complexes Containing the Tripodal Ligand Tris(2-(dimethylamino)ethyl)amine ($trenMe_6$)

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Complexes of the type $[PdX(trenMe_6)]Y$ (where X = Y = Cl, Br, I, or SCN, X = Cl, Br, I, or SCN, and Y = PF_6^- or BPh_4^-; $trenMe_6$ = tris(2-(dimethylamino)ethyl)amine) have been prepared and characterized. In protic and aprotic solvents there is a rapid intramolecular rearrangement involving a five-coordinate and a four-coordinate metal center for all these complexes, and in water one of the *N,N*-dimethylamino groups of the ligand is readily protonated. Although $[Pd(NCS)(trenMe_6)]^+$ was isolated in the solid state, ^1H, ^{13}C, and ^{15}N NMR measurements indicate that in solution it is in equilibrium with its linkage isomer $[Pd(SCN)(trenMe_6)]^+$.

Introduction

We previously reported that the ability of tris(2-(dimethylamino)ethyl)amine, $trenMe_6$, to coordinate to palladium(II) depends on pH and that $[PdCl(trenMe_6H)]Cl_2$ and $[PdCl(trenMe_6)]Cl$ could be isolated from aqueous solutions at pH ~7 and ~12, respectively.[1] The coordinated amine in the former complex functions as a tridentate ligand and as a potentially tetradentate ligand in the latter complex. These complexes have now been investigated further, and a number of new derivatives, $[PdX(trenMe_6)]Y$ (X = Y = Br, I, SCN; X = Cl, Br, I, SCN; Y = PF_6^-, BPh_4^-), have been prepared. We herein report the syntheses together with the results of some physicochemical studies of these palladium(II) complexes.

Experimental Section

Palladium(II) chloride was obtained from Johnson-Matthey and Mallory Ltd. Tris(2-(dimethylamino)ethyl)amine was prepared according to the literature.[2] Anhydrous solvents and freshly dried (100 °C, in vacuo, 24 h) sodium salts were used in the reactions described below.

Proton NMR spectra were recorded on a Varian A60 or a Bruker WP60 spectrometer; ^{13}C and ^{15}N NMR spectra were recorded on a Bruker WH400 spectrometer operating in the FT mode. The ^{13}C chemical shifts were measured at natural abundance; the ^{15}N chemical shifts were measured on an isotopically enriched sample. For the ^1H and ^{13}C NMR spectra, sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) was used as internal reference for aqueous solutions and tetramethylsilane (Me_4Si) for organic solutions; KNO_3 was used as the external reference for the ^{15}N NMR spectra.

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls or KBr disks. Electronic spectra were obtained with a Beckman Acta C III spectrophotometer using 1.0-cm quartz cells. Raman spectra were recorded on a Jarrell-Ash 25-100 spectrophotometer equipped with SSR Model 1105/1120 photon-counting equipment, interfaced to a PDP 11/20 computer. Samples were excited by the 514.5-nm line of a Spectra-physics 165 argon laser operating below 1.0 W.

Electrical conductivities were measured with a Beckman RC 16B2 conductivity bridge at 25 °C using water as the solvent.

Microanalyses were carried out by MHW Laboratories, Phoenix, AZ. Complexes were obtained in 45–80% yields as follows:

Chloro[tris(2-(dimethylamino)ethyl)amine]palladium(II) Chloride, $[PdCl(trenMe_6)]Cl$. This complex was prepared according to the method previously described.[1]

Iodo[tris(2-(dimethylamino)ethyl)amine]palladium(II) Iodide, $[PdI(trenMe_6)]I$. A sample of $[PdCl(trenMe_6)]Cl$ (0.5 g, 1.22 mmol) was dissolved in chloroform (15 mL), and to this solution was added freshly dried NaI (0.45 g, 3.0 mmol). The resulting mixture was then stirred at room temperature for 24 h. The initial yellow solution became violet–red during the course of the reaction. The solution was then filtered by gravity and the residue washed with three 5-mL portions of chloroform. The filtrate and washings were combined, and the solvent was removed with the aid of a roto-evaporator. The remaining residue was then dissolved in the minimum amount of acetone (ca. 5 mL), and hexane (60 mL) was added with constant stirring to precipitate $[PdI(trenMe_6)]I$ as a finely divided dark yellow solid. The complex was collected by filtration, washed with hexane, and dried in vacuo at room temperature. Anal. Calcd for $PdC_{12}H_{30}N_4I_2$: C, 24.41; H, 5.08; N, 9.48; I, 42.99. Found: C, 24.41; H, 5.05; N, 9.60; I, 42.89. Λ_M = 106 Ω^{-1} cm^2 mol^{-1}.

Iodo[tris(2-(dimethylamino)ethyl)amine]palladium(II) Hexafluorophosphate, $[PdI(trenMe_6)]PF_6$. A sample of $[PdI(trenMe_6)]I$ (0.6 g, 1.0 mmol) was dissolved in acetone (15 mL), and to this solution was added a solution of Et_4NPF_6[3] (0.3 g, 1.1 mol) in acetone (10 mL). A light yellow precipitate of Et_4NI formed, which was filtered off. The filtrate was then concentrated and hexane added to precipitate $[PdI(trenMe_6)]PF_6$. The complex was collected by filtration, washed with ca. 6 mL of ice-cold water, and dried in vacuo in the presence of P_4O_{10}. Anal. Calcd for $PdC_{12}H_{30}N_4IPF_6$: C, 23.69; H, 4.93; N, 9.20; I, 20.86. Found: C, 23.72; H, 4.98; N, 9.05; I, 21.17. Λ_M = 101 Ω^{-1} cm^2 mol^{-1}.

Bromo[tris(2-(dimethylamino)ethyl)amine]palladium(II) Bromide, $[PdBr(trenMe_6)]Br$. This complex was prepared according to the method outlined above for $[PdI(trenMe_6)]I$ with the following modifications. The reaction was allowed to proceed for 48 h during which time the solution became intensely yellow. Hexane was added to the concentrated chloroform solution to precipitate the complex. This complex was found to be very hygroscopic and was subsequently handled in a moisture-free atmosphere. Anal. Calcd for $PdC_{12}H_{30}N_4Br_2$: C, 29.03; H, 6.04; N, 11.28; Br, 32.19. Found: C, 28.99; H, 6.15; N, 11.12; Br, 32.22. Λ_M = 112 Ω^{-1} cm^2 mol^{-1}.

(Thiocyanato-*N*)[tris(2-(dimethylamino)ethyl)amine]palladium(II) Thiocyanate, $[Pd(NCS)(trenMe_6)]SCN$. A mixture of $[PdCl(trenMe_6)]Cl$ (1.0 g, 2.4 mmol) and sodium thiocyanate (0.50 g, 6.0 mmol) in chloroform (20 mL) was stirred at room temperature for 48 h during which time the solution became intensely red. The mixture was then filtered, and the residual sodium salts were washed with several small aliquots of chloroform. The solvent was removed with the aid of a roto-evaporator. The residue was then thoroughly dried by using a standard vacuum line to yield a hygroscopic yellow solid, which was dissolved in acetone to form a concentrated solution. Yellow crystals crystallized from solution after 6–8 h. These were collected by filtration and dried in vacuo at room temperature in the presence of P_4O_{10}. Anal. Calcd for $PdC_{14}H_{30}N_6S_2$: C, 37.14; H, 6.62; N, 18.55; S, 14.16. Found: C, 36.82; H, 6.55; N, 18.56; S, 14.25. Λ_M = 88.6 Ω^{-1} cm^2 mol^{-1}.

(Thiocyanato-*N*)[tris(2-(dimethylamino)ethyl)amine]palladium(II) Hexafluorophosphate, $[Pd(NCS)(trenMe_6)]PF_6$. Silver hexafluorophosphate (0.27 g, 1.1 mmol) was added to a solution of $[Pd(NCS)(trenMe_6)]SCN$ (0.45 g, 1.0 mmol) dissolved in acetone (20 mL), and the resulting mixture was stirred in the dark for 12 h. The precipitated AgSCN was removed by gravity filtration (Whatman No. 5 filter paper). The filtrate was concentrated to produce a viscous red liquid residue to which was added three 10-mL portions of hexane. The supernatant liquid was carefully decanted off and the residue

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Table I. ^{1}H NMR Data for the Complexes [PdX(trenMe$_6$)]Y

complex X	complex Y	δ_{CH}	solvent	N isomer/[a] S isomer
Cl	Cl^-	2.52	D_2O	
Br	Br^-	2.60	D_2O	
I	I^-	2.68	D_2O	
I	I^-	2.70	CD_3CN	
Cl	PF_6^-	2.55	CD_3CN	
I	PF_6^-	2.68	CD_3CN	
SCN	SCN^-	2.56 2.63	D_2O	~2
SCN	SCN^-	2.60 2.65	CD_3CN	~10
SCN	SCN^-	2.73 2.80	$(CD_3)_2CO$	*b*
SCN	PF_6^-	2.57 2.65	CD_3CN	~4
SCN	BPh_4^-	2.55	CD_3CN	~8

[a] Ratio of peak areas obtained by electronic integration. [b] Not measurable.

dried in vacuo leaving behind a yellow solid, which was collected, washed with water, and dried in vacuo in the presence of P_4O_{10}. Anal. Calcd for $PdC_{13}H_{30}N_5SPF_6$: C, 28.93; H, 5.56; N, 12.97; S, 5.94. Found: C, 28.91; H, 5.47; N, 12.28; S, 3.88. Λ_M = 97 Ω^{-1} cm^2 mol^{-1}.

(Thiocyanato-*N*)[tris(2-(dimethylamino)ethyl)amine]palladium(II) Tetraphenylborate, [Pd(NCS)(trenMe$_6$)]BPh$_4$. A solution of [Pd(NCS)(trenMe$_6$)]SCN (0.23 g, 0.50 mmol) in water (10 mL) was prepared. A solution of sodium tetraphenylborate (0.20 g, 0.58 mmol) dissolved in 5 mL of water was then added to immediately produce a precipitate. The mixture was stirred for 30 min at room temperature and the product collected by filtration, washed with cold water, and dried in vacuo. Anal. Calcd for $PdC_{37}H_{50}N_5BS$: C, 62.26; H, 7.00; N, 9.80; S, 4.49. Found: C, 62.15; H, 7.22; N, 9.81; S, 3.73.

Chloro[tris(2-(dimethylamino)ethyl)amine]palladium(II) Hexafluorophosphate, [PdCl(trenMe$_6$)]PF$_6$. Silver hexafluorophosphate (1.0 g, 2.4 mmol) was added to a suspension of [PdCl(trenMe$_6$)]Cl (1.0 g, 2.4 mmol) in dry acetone (25 mL), and the resulting mixture was stirred at room temperature for 12 h in the absence of light. The silver chloride that formed was filtered off and the solvent removed from the yellow filtrate by using a roto-evaporator. The remaining crystalline residue was washed with hexane and finally with two 5-mL portions of ice-cold water. The compound was dried in vacuo at room temperature. Anal. Calcd for $PdC_{12}H_{30}N_4ClPF_6$: C, 27.88; H, 5.80; N, 10.83; Cl, 6.85. Found: C, 27.75; H, 5.82; N, 10.86; Cl, 6.88. Λ_M = 128 Ω^{-1} cm^2 mol^{-1}.

(Thiocyanato-*N*)[bis(2-(dimethylamino)ethyl)(2-(dimethylammonio)ethyl)amine]palladium(II) Hexafluorophosphate, [Pd(NCS)(trenMe$_6$H)](PF$_6$)$_2$. A solution of [Pd(NCS)(trenMe$_6$)]SCN (0.45 g, 1.0 mmol) in water (10 mL) was prepared, and to this solution was slowly added an aqueous solution (10 mL) of $NaPF_6$ (0.4 g, 2.4 mmol). A precipitate formed immediately, which was filtered, washed with water, and dried in vacuo in the presence of P_4O_{10}. Anal. Calcd for $C_{13}H_{31}F_{12}N_5P_2SPd$: C, 22.77; H, 4.52; N, 10.21; S, 4.67. Found: C, 22.17; H, 4.79; N, 9.86; S, 4.56.

Bromo[bis(2-(dimethylamino)ethyl)(2-(diethylammonio)ethyl)amine]palladium(II) Hexafluorophosphate, [PdBr(trenMe$_6$H)](PF$_6$)$_2$. This was prepared by using $NaPF_6$ and [PdBr(trenMe$_6$)]Br as outlined above for [Pd(NCS)(trenMe$_6$H)](PF$_6$)$_2$. Anal. Calcd for $C_{12}H_{31}BrF_{12}N_4P_2Pd$: C, 20.37; H, 4.38; N, 7.91; Br, 11.29. Found: C, 21.51; H, 4.92; N, 8.09; Br, 11.37.

[Pd(^{15}NCS)(trenMe$_6$)]SC^{15}N. This was prepared according to the procedure used for [Pd(NCS)(trenMe$_6$)]SCN with $NaSC^{15}N$ (99 atom %).

Results and Discussion

The diamagnetic complexes [PdX(trenMe$_6$)]X (X = Br, I, or SCN) were prepared by metathesis according to reaction 1 using $CHCl_3$ as solvent. Complexes of the type [PdX(trenMe$_6$)]Y (Y = PF_6^- or BPh_4^-) were obtained by anion exchange using the appropriate amount of $AgPF_6$, Et_4NPF_6, or $NaBPh_4$ in acetone.

$$[PdCl(trenMe_6)]Cl + 2NaX \rightarrow [PdX(trenMe_6)]X + 2NaCl \quad (1)$$

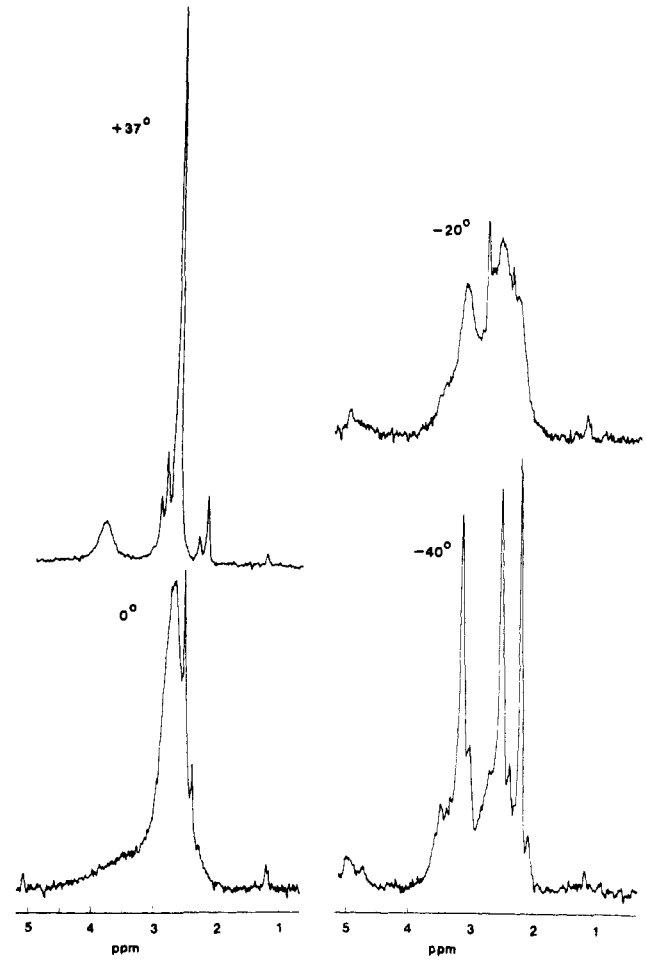
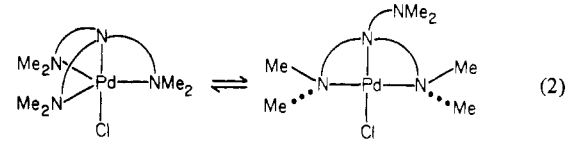


Figure 1. Proton NMR spectra of [PdCl(trenMe$_6$)]Cl in CD_2Cl_2 at various temperatures.

^{1}H NMR Data. The ^{1}H NMR spectra of [PdX(trenMe$_6$)]$^+$ (X = Cl, Br, or I) exhibit a sharp singlet for the resonance due to the methyl protons in both a protic solvent (D_2O) and an aprotic solvent ($CDCl_3$ or CD_2Cl_2). The pertinent chemical shifts are presented in Table I. A single line for the methyl protons is consistent with the presence of a rapid equilibrium (on the NMR time scale) between the five-coordinate (trigonal-bipyramidal) species **1** and the four-coordinate (square-planar) species **2** shown in eq 2.[1]



1 **2**

This equilibrium was examined further by recording the ^{1}H NMR spectra of [PdCl(trenMe$_6$)]Cl in CD_2Cl_2. In this solvent the "free arm" of the ligand in **2** is not protonated and [PdCl(trenMe$_6$H)]$^{2+}$ is not present in solution. Spectra obtained between +37 and −40 °C are shown in Figure 1. As the temperature is lowered from 37 °C, the singlet at 2.68 ppm collapses, and at −40 °C, three sharp singlets of approximately equal intensity appear at 3.30, 2.60, and 2.26 ppm, which are superimposed on the methylene proton resonances. When the solution was allowed to warm up to 37 °C, the original spectrum was observed.

The low-temperature spectrum is consistent with the square-planar cation **2** as the only detectable species in solution. There are three pairs of magnetically nonequivalent methyl groups—the methyl groups of the uncoordinated dimethyl-

Table II. Infrared and Raman Spectral Data for [Pd(CNS)(trenMe$_6$)]Y

complex	ν_{CN}, cm^{-1} IR	ν_{CN}, cm^{-1} Raman	ν_{CS}, cm^{-1} IR	ν_{CS}, cm^{-1} Raman
[Pd(NCS)(trenMe$_6$)]SCN	2105	2103	834	834
	2060[a]	1056[a]	742[a]	741[a]
[Pd(NCS)(trenMe$_6$)]PF$_6$	2112		[b]	
[Pd(NCS)(trenMe$_6$)]BPh$_4$	2098		[b]	

[a] Ionic SCN$^-$. [b] ν_{CS} obscured by anion absorptions.

amino moiety, two methyl groups above the square plane of **2**, and two methyl groups below the square plane of **2**. Since the methyl resonance of the free ligand occurs at 2.08 ppm and the chemical shift for the methyl protons of the coordinated dimethylamino groups of [PdCl(trenMe$_6$H)]$^{2+}$ [1] occurs at about 3.0 ppm, we assign the high-field singlet (2.26 ppm) to the uncoordinated dimethylamino groups of **2** and the remaining two signals to the coordinated dimethylamino groups. Clearly, the rate of the intramolecular rearrangement process given in eq 2 is significantly retarded at low temperatures, and the equilibrium is shifted to the right in favor of the four-coordinate species. This is not surprising in view of the fact that the most common coordination number exhibited by Pd(II) is 4.

The tripodal stereochemistry of trenMe$_6$ normally induces a five-coordinate geometry about a metal center in the solid state.[4-6] However, all five-coordinate complexes of the type [MX(trenMe$_6$)]X that have been reported to date have had a high-spin metal center, which has precluded any ^{1}H NMR spectral measurements, and consequently a rearrangement process similar to that in eq 2 has not previously been observed.

[PdX(trenMe$_6$)]$^{2+}$ (X = SCN). Linkage isomers having Pd–NCS or Pd–SCN bonds are possible when X = SCN.[7] The presence of six methyl groups in the ligand is expected to sterically favor a linear Pd–NCS bond rather than a bent Pd–SCN bond,[8] and the infrared and Raman data for [PdCNS(trenMe$_6$)]SCN[9] are consistent with the presence of only the N-bonded isomer in the solid state.[10] Relevent spectral data are given in Table II.

The infrared data in Table II also suggest that the size of the counteranion does not alter the nature of the donor atom of the thiocyanato ligand in the solid state since the ν_{CN} frequency does not change significantly with a change in the counteranion (SCN$^-$, PF$_6^-$, or BPh$_4^-$). This observation is contrary to what has been observed for [Pd(CNS)(Et$_4$dien)]Y complexes, where Y = SCN$^-$, PF$_6^-$, or BPh$_4^-$ and Et$_4$dien = Et$_2$NC$_2$H$_4$NHC$_2$H$_4$NEt$_2$.[11] For these particular complexes the N-bonded isomer is preferred in the solid state when Y = SCN$^-$ or PF$_6^-$ while the S-bonded isomer is favored when Y = BPh$_4^-$.

The ^{1}H NMR spectrum of [Pd(CNS)(trenMe$_6$)]SCN in D$_2$O unexpectedly showed *two* singlets for the methyl protons at 2.63 and 2.71 ppm with peak areas in a ratio less than 2. The relative areas were also found to be independent of the concentration of [Pd(CNS)(trenMe$_6$)]$^{2+}$. The spectrum did not change in the presence of added KSCN nor did it dramatically change as the temperature was raised to about 85 °C. These results preclude an equilibrium such as that given by eq 2 as well as exchange of coordinated thiocyanate from occurring in solution. However, these results suggest the presence of an equilibrium involving two linkage isomers as shown in eq 3. This equilibrium is slow on the NMR time

$$[Pd(NCS)(trenMe_6)]^+ \rightleftharpoons [Pd(SCN)(trenMe_6)]^+ \quad (3)$$

scale, and presumably a rapid equilibrium analogous to that given by eq 2 is also occurring at the same time for each of the linkage isomers.

Table III. ^{13}C and ^{15}N Chemical Shift Data for [Pd(CNS)(trenMe$_6$)]SCN in D$_2$O

complex	^{13}C δ[a]	^{15}N δ[b]
[Pd(NCS)(trenMe$_6$)]SCN	132.7	−193.4
[Pd(SCN)(trenMe$_6$)]SCN	123.4	−298.6

[a] Chemical shift for noncoordinated SCN$^-$ observed at 133.8 ppm. [b] Chemical shift for noncoordinated SCN$^-$ observed at −219.2 ppm.

The ^{1}H NMR spectrum of [Pd(CNS)(trenMe$_6$)]$^+$ is markedly solvent dependent, and the relative intensity of the downfield methyl resonance decreased significantly when the solvent was changed from D$_2$O to acetonitrile-d_3 or acetone-d_6. In acetone-d_6 the downfield signal virtually disappeared from the spectrum.

All other things being equal, it seems reasonable to assume, as observed for four-coordinate palladium(II) complexes,[12] that the S-bonded isomer would be favored in a solvent having a high dielectric constant when compared to a solvent with a low dielectric constant. Accordingly, from the data in Table I we may conclude that the low-field methyl resonance is due to the S-bonded isomer and the high-field resonance is due to the N-bonded isomer.

The methyl resonances, however, are not sufficiently separated to allow a precise measure of their relative areas, and only approximate values of the ratio of N-bonded isomer to S-bonded isomer could be obtained. These are given in Table I and show that there is no apparent correlation between the relative amounts of the two isomers in solution and the nature of the counteranion in a given solvent.

In order to unequivocally confirm the presence of equilibrium 3 and the assignment of the methyl resonances, the ^{13}C and ^{15}N NMR spectra of [Pd(CNS)(trenMe$_6$)]SCN were recorded. Recent studies have indicated that these NMR probes should be useful in making assignments of the bonding mode of coordinated thiocyanate.[13,14] The chemical shift data are given in Table III.

Two ^{13}C chemical shifts for coordinated thiocyanate were observed at 132.7 and 123.4 ppm relative to DSS with peak areas in a ratio of about 1.6, which confirm the presence of two linkage isomers in solution. The larger chemical shift is due to the N-bonded isomer and the smaller chemical shift to the S-bonded isomer. We find that for our complexes the chemical shift of *ionic* thiocyanate is downfield of N-bound thiocyanate, representing an exception to the generalization reported earlier[13] in which these chemical shifts increase from tetramethylsilane in the order N-bound ≥ ionic > S-bound.

Two ^{15}N chemical shifts were also observed for coordinated

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(8) K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", W. B. Saunders Co, Philadelphia, PA, 1977, p 618.
(9) Written discussions pertaining to coordinated thiocyanate often refer to the formalism M(CNS) when there is no intent to specify the nature of the donor atom (N or S). This formalism is also used throughout this paper. See, for example, J. J. MacDougall, J. H. Nelson, M. W. Babich, C. C. Fuller, and R. A. Jacobson, *Inorg. Chim Acta*, **27**, 201 (1978), and references therein.
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Table IV. Electronic Spectral Data for the Complexes $[PdX(trenMe_6)]Y$

complex			
X	Y	λ_{max}, nm	ϵ_{max}, L mol^{-1} cm^{-1}
Cl	Cl	358[a]	714[a]
Cl	Cl	346[a]	714[b]
Br	Br	375[a]	476[a]
Br	Br	352[b]	792[b]
I	I	430[a]	710[a]
I	I	414[b]	625[b]
Cl	PF_6	357[c]	666[c]
I	PF_6	425[c]	700[c]
SCN	SCN	263[b]	7156[b]
		325[b]	1833[b]
SCN	SCN	267[d]	3788[d]
		338[d]	1944[d]
SCN	PF_6	268[a]	3374[a]
		346[a]	1380[a]
SCN	BPh_4	265[d]	6250[d]
		336[d]	1450[d]

[a] CH_2Cl_2. [b] H_2O. [c] $(CH_3)_2CO$. [d] CH_3CN.

thiocyanate. These occur at −193.4 and −298.6 ppm relative to KNO_3. In this case the ratio of the areas of these two signals was 1.7. Thus, the chemical shift upfield (−298.6 ppm) is due to the S-bonded isomer, and the chemical shift downfield (−193.4 ppm) is due to the N-bonded isomer.

Contrary to other complexes of the type $[MX(trenMe_6)]X$,[4-6] which are five-coordinate in the solid state, $[Pd(NCS)(trenMe_6)]SCN$ has been shown to contain a four-coordinate palladium(II) center with $trenMe_6$ functioning as a tridentate ligand with one uncoordinated dimethylamine group.[15] Undoubtedly, the propensity of Pd(II) to be four-coordinate and packing effects suppress the ability of $trenMe_6$ to behave as a tetradentate ligand and form a five-coordinate complex in the solid state.

Attempts To Prepare $[PdX(trenMe_6)]PF_6$ (X = Br, SCN). Attempts to replace the counteranion of $[PdBr(trenMe_6)]Br$ and $[PdNCS(trenMe_6)]SCN$ with PF_6^- by using an aqueous solution of $NaPF_6$ resulted in the formation of the four-coordinate derivatives $[PdX(trenMe_6H)](PF_6)_2$ according to eq 4. This behavior was previously noted for aqueous solutions of $[PdCl(trenMe_6)]^+$ in the presence of BF_4^- or ClO_4^- ions.[1]

$$[PdX(trenMe_6)]X + 2NaPF_6 + H_2O \rightarrow [PdX(trenMe_6H)](PF_6)_2 + NaX + NaOH \quad (4)$$

The ^1H NMR spectra of the protonated hexafluorophosphate salts in CD_3CN or $(CD_3)_2CO$ were identical with those of the corresponding nonprotonated derivatives, indicating that there is essentially complete dissociation of the acidic hydrogen (eq 5). The position (2108 cm^{-1}) and width

$$[PdX(trenMe_6H)]^{2+} \rightarrow [PdX(trenMe_6)]^+ + H^+ \quad (5)$$

of the ν_{CN} band in the spectrum of $[Pd(CNS)(trenMe_6H)](PF_6)_2$ are consistent with the presence of a Pd–NCS bond in the solid state.

When sodium tetraphenylborate was used in place of sodium hexafluorophosphate, $[Pd(NCS)(trenMe_6)]BPh_4$ precipitated from solution. The precise reasons for this behavior are not clear at present, but the size of the anion is presumably an important factor.[16]

Electronic Spectra. Data are given in Table IV. The $[PdX(trenMe_6)]^+$ ions (X = Cl, Br, or I) are characterized by an absorption band in the visible region that increases in energy as X is varied from I to Br to Cl. These absorption bands may be assigned to the d–d electronic transition.[17]

$(xz, yz)^4(xy, x^2-y^2)^4 \rightarrow (xz, yz)^4(xz, x^2-y^2)^3(z^2)^1$ ($^1A'_1 \rightarrow {}^1E'$) for C_{3v} symmetry. The corresponding band when X = SCN occurs at somewhat higher energy (ca. 30 700 cm^{-1}) and has gained intensity by virtue of its proximity to the other intense band at ca. 45 450 cm^{-1}. This high-energy band may be assigned to a charge-transfer electronic transition involving the metal center and the ligand. However, it is not possible at present to unambiguously assign this band to either a metal-to-ligand (M → L) or a ligand-to-metal (L → M) transition.

Conclusions. The results reported here demonstrate that $N(CH_2CH_2N(CH_3)_2)_3$, $trenMe_6$, can function as either a tri- or tetradentate ligand and that for palladium(II) this depends on whether or not the solid or solution phase is being considered. In addition, this study has shown that ^{13}C and ^{15}N NMR can be used effectively to assign the bonding mode of coordinated thiocyanate.

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Registry No. $[PdCl(trenMe_6)]Cl$, 83418-07-9; $[PdI(trenMe_6)]I$, 83418-08-0; $[PdI(trenMe_6)]PF_6$, 85335-22-4; $[PdBr(trenMe_6)]Br$, 83418-09-1; $[Pd(NCS)(trenMe_6)]SCN$, 71744-83-7; $[Pd(NCS)(trenMe_6)]PF_6$, 85335-23-5; $[Pd(NCS)(trenMe_6)]BPh_4$, 85335-24-6; $[PdCl(trenMe_6)]PF_6$, 68448-31-7; $[Pd(NCS)(trenMe_6H)](PF_6)_2$, 85335-25-7; $[PdBr(trenMe_6H)](PF_6)_2$, 85335-28-0; $[Pd(SCN)(trenMe_6)]^+$, 85335-29-1.

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