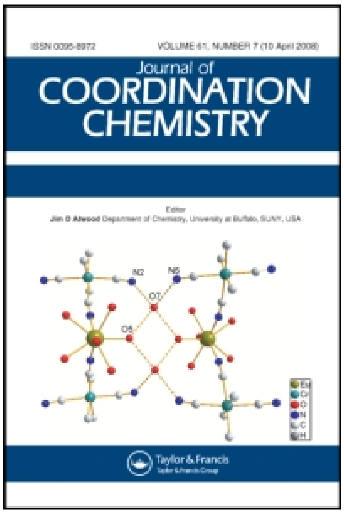

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REACTION OF TETRACHLOROPALLADATE(II) WITH *BIS*(2-CHLOROETHYL)AMINE: SELECTIVE FORMATION OF A *trans* ISOMER. CRYSTAL STRUCTURE OF *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$

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On reacting $[PdCl_4]^{2-}$ with *bis*(2-chloroethyl)amine, *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**) results selectively in high yield (~80%). The structure of **1** has been solved by X-ray diffraction methods. The immediate environment about palladium is slightly distorted square planar. Pd–Cl bond lengths (2.297(1)/2.999(1) Å) are in accordance with the *trans*-influence of various co-ligands. The Pd–N bond length is intermediate between Pd–NH_3 and Pd–NMe_2 bond distances. Attempts to substitute the Cl atom of the alkyl chain by the nucleophile $ArTe^-$ leads to dissociation of the complex resulting in $Pd(TeAr)_2$ and $NH(CH_2CH_2TeAr)_2$.

Keywords: *bis*(2-chloroethyl)amine; crystal structure; palladium; *trans*-isomer

INTRODUCTION

In square planar complexes of palladium/platinum(II) relative *trans*-effects of various ligands may be used to predict products of substitution and select synthetic routes for various isomers.[1] The reactions of $PdCl_4^{2-}$ and $PtCl_4^{2-}$ with non-bulky alkylamines are generally expected to give a *cis* isomer due

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* Corresponding author.

to the greater *trans* influence of Cl. The kinetic lability of Pd(II) complexes is greater than that of Pt(II) analogues and the thermodynamic stability of the *trans* isomer is also high. Both these factors result in the formation of the *trans* isomer in case of Pd(II) in spite of the greater *trans* influence of Cl. Reaction of $PdCl_4^{2-}$ with *bis*(2-chloroethyl)amine gives a *trans* isomer in very high yield (> 80%). Formation of this *trans* isomer has been verified by solving the crystal structure of the reaction product. Details of the selective synthesis of *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ and its crystal structure are given below.

EXPERIMENTAL

$NH(CH_2CH_2OH)_2$ (E. Merck, India) was chlorinated[2] with thionyl chloride to prepare *bis*(2-chloroethyl)amine. Na_2PdCl_4 (Aldrich, USA) was used as received. Elemental analyses were carried out on a Perkin-Elmer 240C instrument. IR spectra were recorded in the range 200–4000 cm^{-1} in CsI discs on a Nicolet 5DX FT-IR spectrophotometer.

Synthesis of *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (1)

Na_2PdCl_4 (1 mmol) was dissolved in hot methanol and mixed with a solution of *bis*(2-chloroethyl)amine hydrochloride (2 mmol or in excess) in methanol. The mixture was stirred for 1 h and concentrated under reduced pressure. The reddish yellow solid which formed was filtered and crystals (pale-yellow) were grown from $CHCl_3$: MeOH (8 : 2) mixture. Yield ~80%. M.P. 152–154°C. Analyses: Found: C, 21.35; H, 4.23; Calc.: C, 20.82; H, 3.90%. IR : ν(Pd–Cl), 345 cm^{-1}.

X-ray Diffraction Analysis

A pale yellow blocky crystal of $[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**) was mounted on a glass fibre and sealed with epoxy glue. Data were collected on a Siemens SMART/CCD system with graphite-monochromated MoKα radiation. Cell constants corresponded to a monoclinic cell whose dimensions are given in Table I along with other experimental parameters. A semiempirical absorption correction gave no improvement to the refinement and the correction was not applied.

The structure was solved by direct methods.[3] The non-hydrogen atoms, other than carbon, were refined anisotropically. The hydrogen atoms were included in idealized positions, with C–H set at 0.95 Å, and the positions of the hydrogen atoms attached to nitrogen were found from a difference

TABLE I Crystallographic data for *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**)

Compound	$PdCl_2[NH(CH_2CH_2Cl)_2]_2$ **1**
Formula	$C_8H_{18}N_2Cl_6Pd$
M	461.36
Space group	$P2_1/c$
a/Å	10.086(1)
b/Å	12.589(1)
c/Å	13.798(1)
β/°	99.442(1)
U/Å^3	1724.4(4)
Z	4
D_c/g cm^{-3}	1.78
F_{000}	912.00
μ(MoKα)/mm^{-1}	1.99
2θ max/°	50
Reflections	$\pm h, +k, +l,$
measured	2464
observed $[F_o^2 \geq 3\sigma(F_o)^2]$, N_o	1903
No. of parameters refined, N_p	154
Largest shift/e.s.d. in final cycle	0.001
Largest electron-density peak/e Å^{-3}	0.44
R^a	0.0294
R_w^b	0.0352
Goodness of fit, ^cS	2.17

$^aR = \sum||F_o| - |F_c||/\sum|F_o|$; $^bR_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$, where $w = 1/\sigma^2(F_o)$; $^cS = [\sum(|F_o| - |F_c|)/\sigma]/(N_o - N_p)$.

Fourier map and then fixed with isotropic thermal parameters set at 1.2 times that of the atom to which they were attached. The final cycle of full-matrix least-squares refinement[4] was based on 1903 observed reflections ($I > 3.00\sigma(I)$) and 154 variable parameters and converged (largest parameter shift was 0.001 times its e.s.d.) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.029$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.0352$.

The standatd deviations of an observation of unit weight[5] was 2.17. Plots of $\sum w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.44 and -0.54 e/Å^3, respectively. Neutral-atom scattering factors were taken from Croner and Waber.[6] Anomalous dispersion effects were included in F_c.[7] The values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[8] All calculations were performed using the TEXSAN[9] crystallographic software package of Molecular Structure Corporation.

Final atomic coordinates of the non-hydrogen atoms are given in Table II, important distances and bond angles in Table III and an ORTEP diagram is in Figure 1. Additional material available from the authors comprises H-atom coordinates, thermal parameters and lists of observed and calculated structure factors.

TABLE II Atomic coordinates and *B*(eq) of non-hydrogen atoms for *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**)

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Pd(1)	0.252066(28)	0.222201(28)	0.252998(20)	3.83(2)
Cl(1)	0.39830(11)	0.158008(94)	0.155595(78)	5.25(6)
Cl(2)	0.10643(12)	0.285924(98)	0.351254(87)	5.86(6)
Cl(3)	0.67799(13)	0.25813(12)	0.36636(10)	6.97(7)
Cl(4)	0.41900(13)	0.45427(12)	0.09079(10)	7.13(7)
Cl(5)	−0.17824(12)	0.18436(12)	0.14150(11)	7.21(7)
Cl(6)	0.08610(15)	−0.01582(14)	0.40900(11)	8.20(9)
N(1)	0.38322(30)	0.34670(27)	0.29210(23)	4.3(2)
N(2)	0.11953(31)	0.09905(29)	0.21139(24)	4.6(2)
C(1)	0.44324(46)	0.34807(44)	0.39717(34)	6.0(3)
C(2)	0.53152(51)	0.25729(49)	0.42655(35)	6.6(3)
C(3)	0.32117(50)	0.45090(41)	0.26269(40)	6.1(3)
C(4)	0.27953(46)	0.45969(40)	0.15447(46)	6.8(3)
C(5)	0.05938(47)	0.10212(47)	0.10689(36)	6.5(3)
C(6)	−0.03118(52)	0.19283(55)	0.08218(37)	7.4(3)
C(7)	0.17854(50)	−0.00798(43)	0.23675(42)	6.3(3)
C(8)	0.22412(47)	−0.02155(42)	0.34307(47)	7.1(3)

TABLE III Bond lengths (Å) and angles (°) for *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**)[a]

Pd(1)–Cl(1)	2.297(1)	Pd(1)–Cl(2)	2.299(1)
Pd(1)–N(1)	2.065(3)	Pd(1)–N(2)	2.066(6)
N(1)–C(1)	1.474(5)	N(2)–C(5)	1.467(6)
N(1)–C(3)	1.481(6)	N(2)–C(7)	1.491(6)
N(1)–H(1)	0.98	N(2)–H(2)	0.99
C(1)–C(2)	1.464(7)	C(5)–C(6)	1.467(7)
C(3)–C(4)	1.484(7)	C(7)–C(8)	1.471(7)
C(2)–Cl(3)	1.809(5)	C(6)–Cl(5)	1.810(5)
C(4)–Cl(4)	1.777(5)	C(8)–Cl(6)	1.784(5)
Cl(1)–Pd(1)–Cl(2)	179.66(4)	N(1)–Pd(1)–N(2)	178.9(1)
Cl(1)–Pd(1)–N(1)	88.51(8)	Cl(2)–Pd(1)–N(2)	88.75(9)
Cl(1)–Pd(1)–N(2)	91.28(9)	Cl(2)–Pd(1)–N(1)	91.47(9)
Pd(1)–N(1)–C(1)	114.0(3)	Pd(1)–N(2)–C(5)	113.4(3)
Pd(1)–N(1)–C(3)	112.2(3)	Pd(1)–N(2)–C(7)	113.4(3)
Pd(1)–N(1)–H(1)	101.9	Pd(1)–N(2)–H(2)	104.1
C(1)–N(1)–C(3)	110.2(4)	C(5)–N(2)–C(7)	109.8(4)
C(1)–N(1)–H(1)	107.6	C(5)–N(2)–H(2)	110.3
C(3)–N(1)–H(1)	110.6	C(7)–N(2)–H(2)	105.4
N(1)–C(1)–C(2)	113.3(4)	N(2)–C(5)–C(6)	112.9(4)
N(1)–C(3)–C(4)	112.2(4)	N(2)–C(7)–C(8)	112.7(4)
C(1)–C(2)–Cl(3)	112.0(4)	C(5)–C(6)–Cl(5)	112.0(4)
C(3)–C(4)–Cl(4)	112.1(4)	C(7)–C(8)–Cl(6)	111.1(3)

[a] No e.s.d. involving H(1) and H(2) because positions were fixed.

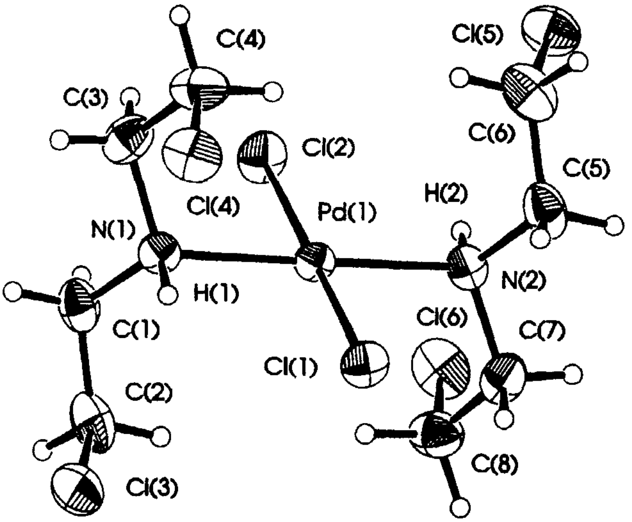

FIGURE 1 ORTEP plot of the molecule *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**). The non-hydrogen atoms are drawn with 30% probability ellipsoids.

RESULTS AND DISCUSSION

We have a current interest in the chemistry of symmetrical bidentate, hybrid bidentate and polydentate organotellurium ligands.[10–14] In continuation of these studies we were attempting to synthesize a cyclic system, potentially a (Te_3, N_3) donor, by reacting Na_2Te (generated *in situ* by borohydride reduction of elemental tellurium) with equimolar amounts of *bis*(2-chloroethyl)amine. The product obtained in this attempt was found to be very unstable and it was reacted with $PdCl_4^{2-}$, in the hope of stabilizing the new ring system *via* coordination with palladium. However, from the reaction mixture we could crystallize only *trans*-$[PdCl_2\{NH(CH_2CH_2Cl)_2\}_2]$ (**1**) in good yield. Probably the unstable cyclic derivative gave back the amine which ultimately reacted with Pd(II). Later, independent reaction of $PdCl_4^{2-}$ with $NH(CH_2CH_2Cl)_2$ as described also gave the same product. The crystal structure of **1** has been solved by X-ray diffraction methods. The *trans* isomer is the main product of the reaction, whereas on the basis of *trans*-effect alone such a reaction is expected to give a *cis* isomer predominantly. The presence of Cl at the end of each alkyl chain linked with nitrogen reduces the σ-donor capability of nitrogen and therefore enhances the lability of the complex which results in the formation of a *trans* isomer selectively. This may also happen due to steric effects but strong steric interactions with the ethyl group are unexpected.

Fresh crystals of **1** are soluble in organic solvents such as chloroform, dichloromethane, methanol, ethanol, DMF and DMSO. However, for crystals which are more than 4 months old, solubility diminishes significantly.

The immediate environment about palladium in this complex is slightly distorted square planar (Figure 1). C5 and C7 are more symmetrically placed with respect to the N1–Pd–N2 axis than are C1 and C3. The Pd–Cl bond length in the present complex is shorter than the value (2.39(2)–2.42(2) Å) when it is *trans* to tellurium,[10] but somewhat longer in comparison to Pd–Cl (2.287(3) Å) which is *trans* to pyridine.[12] The Pd–Cl bond (2.394(3)–2.415(3) Å) *trans* to phosphorus is also longer[15] than the Pd–Cl distances observed in the present complex. These observations are in agreement with the higher *trans* influence of Cl than pyridine and further suggests that *trans* influences of PPh_2 and ArTe groups are comparable and greater than of Cl. Pd–N bond lengths of the present complex are within the range observed for this bond (1.90–2.15 Å). However, they are between $Pd–NH_3$ (2.02 Å)[16] and $Pd–NMe_2$ (2.13 Å) bond lengths reported recently.[17,18]

Reaction of **1** with the nucleophile $ArTe^-$ was studied in methanol. It was observed that $Pd(TeAr)_2$ and $NH(CH_2CH_2TeAr)_2$[19] are formed in this reaction and nucleophilic substitution of Cl by $ArTe^-$ cannot be carried out, keeping the complex intact.

Acknowledgments

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[4] Least-squares function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2(F_o^2)$; $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2](Lp)^2$, $S =$ scan rate, $C =$ total integrated peak count, $R =$ ratio of scan time to background counting time, $Lp =$ Lorentz–polarization factor, and $p = p$ factor.

[5] Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/N_o - N_V]^{1/2}$, where $N_o =$ number of observations and $N_V =$ number of variables.

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