work, we have proved the paramagnetism of WCp_2. As our experiments showed,[3] the two unpaired electrons need not pose a bar to reactivity, because the large spin-orbit coupling constants of the heavy metals provide a mechanism of intersystem crossing. On the contrary, their presence may be conducive to C–H activation. In future experiments, it will be important to test for paramagnetism in other C–H-activating intermediates.

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Registry No. $MoCp_2H_2$, 1291-40-3; WCp_2H_2, 1271-33-6; $W(MeCp)_2H_2$, 61112-90-1; $W(MeCp)_2Cl_2$, 63374-11-8; $W(MeCp)_2(C_2H_4)$, 87433-04-3; $W(MeCp)_2$, 87433-05-4; $EtAlCl_2$, 563-43-9.

Contribution from the Cancer Research Campaign Biomolecular Structure Research Group, Department of Biophysics, King's College, London WC2B 5RL, England, and Department of Chemistry, Birkbeck College, London WC1E 7HX, England

Crystal and Molecular Structure of Three Isomers of Dichlorodiamminedihydroxoplatinum(IV): Cis–Trans Isomerization on Recrystallization from Water

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The structures of the cis,cis,trans (compound I), trans,trans,trans (compound II), and cis,trans,cis (compound III) isomers of $PtCl_2(NH_3)_2(OH)_2$ have been determined by X-ray diffraction. In addition, I has been characterized in solution by ^{15}N and ^{195}Pt NMR. All compounds have closely octahedral coordination geometry for Pt(IV), normal Pt–O, Pt–N, and Pt–Cl distances, and extensive H-bonding networks in the crystals. A curious isomerization of II to III was observed on recrystallization from water but not from H_2O_2 solutions. This facile conversion was confirmed by X-ray crystallography and infrared spectroscopy.

There is considerable interest in the antitumor activity of Pt(IV) diammine complexes.[1] In some animal test systems they show superior activity to their Pt(II) analogues; for example, the therapeutic index for *cis,cis,trans*-$PtCl_2(NH_3)_2(OH)_2$ against the ADJ/PC6 tumor in BALB/C mice (28.1) is much higher than that for *cis*-$PtCl_2(NH_3)_2$ (8.1).[2] The axial hydroxyl groups often confer additional solubility on the complex, but in vivo it is suspected that they may be removed by reduction of the Pt(IV) complex to Pt(II). There is currently little evidence for this, although we have shown that thiols such as cysteine readily reduce *cis,cis,trans*-$PtCl_2(i\text{-}PrNH_2)_2(OH)_2$ in tissue culture media.[3]

There is little structural data available on Pt(IV) diammine complexes, and therefore we have embarked upon a study of the structures of the hydrogen peroxide oxidized adducts of Pt(II) diammine antitumor complexes both in the solid state and in solution, using primarily a combination of X-ray crystallography and multinuclear NMR spectroscopy. Our initial aim was to compare *cis,cis,trans*- and *trans,trans,trans*-$PtCl_2(NH_3)_2(OH)_2$ (compounds I and II, respectively). It was during the recrystallization of the latter complex from water that we discovered an unexpectedly facile isomerization involving the chloride and hydroxo ligands to produce a third isomer *cis,trans,cis*-$PtCl_2(NH_3)_2(OH)_2$ (compound III). Pt(IV) complexes are usually considered to be kinetically inert in solution.

Additional interest in platinum hydroxo complexes has been stimulated by the work of Rosenberg and Lock.[4,5] When our work was almost complete, we learned that they had also studied the crystal structure and vibrational spectra of compound I, and we therefore report our work only briefly where there is overlap.

Experimental Section

Compounds I and II were prepared by published procedures[6] involving the oxidation of *cis*- and *trans*-$PtCl_2(NH_3)_2$ with H_2O_2.

Table I. Infrared Data (cm^{-1}) for Isomers of $PtCl_2(NH_3)_2(OH)_2$[a]

cis,cis,trans (I)	trans,trans,trans (II)	cis,trans,cis (III)	assignt[b]
3510 (s)	3510 (s)	3460 (s)	ν(OH)
3255 (s)	3310 (s)	3290 (m)	
2950 (br, m)	3060 (s, br)	3200	
	2960 (s, br)	3120 (m, br)	$\nu(NH_3)$
		3040	
2600 (s)	2680 (m)		
		2560 (m)	
2425 (m)		2420 (w)	
2240 (m)	2270 (w)	2290 (w, br)	
2180 (m)	1950 (w, br)		
	1770 (w, br)		
1590 (w)	1620 (m)	1615 (m)	$\delta(NH_3)$
1560 (w, br)	1600 (m)	1580 (m, br)	
	1560 (m)		
1415 (w)	1355 (m)	1345 (m)	
1300 (w)			
1270 (w)		1255 (m)	
1165 (m)	1170 (s)		
1105 (w)			
1040 (m)	960 (w)	1075 (m)	δ(PtO–H)
	905 (w)		
765 (m)		800 (w)	
690 (w)			
	568 (s)	580 (s)	
540 (s)	530 (m, sh)	535 (m, sh)	ν(PtO), ν(PtN)
505 (sh, m)	505 (m, br)	505 (m)	
445 (m, br)			
330 (s)	350 (m)	335 (s)	ν(PtCl)
	325 (m)		
275 (m)	290 (m, sh)		
	272 (m)		

[a] s = strong; m = medium; w = weak; sh = shoulder; br = broad.
[b] See ref 5.

Anal. Calcd: H, 2.39; N, 8.39; Cl, 21.25. Found (I): H, 2.36; N, 8.39; Cl, 21.14. Found (II): H, 2.20; N, 8.43; Cl, 21.37. Found

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[‡] Birkbeck College.

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Table II. Crystal Data and Conditions of Data Collection and Structure Refinement

	I	II	III
fw	334.07	334.07	334.07
cryst syst	tetragonal	monoclinic	monoclinic
a, Å	7.339 (1)	5.974 (1)	6.422 (2)
b, Å		6.807 (1)	7.478 (2)
c, Å	11.376 (2)	8.232 (2)	6.615 (1)
β, deg		106.5 (1)	90.87 (1)
V, Å^3	612.7 (2)	321.1 (3)	317.7 (2)
d_{calcd}, g cm^{-3}	3.621	3.456	3.492
d_{measd}, g cm^{-3}	>2.8	>2.8	>2.8
Z	4	2	2
F(000)	600	300	300
space group	$P4_2/n$	$P2_1/c$	$P2_1/m$
μ(Mo Kα), cm^{-1}	248.5	237.1	239.6
cryst size, mm	0.25 × 0.25 × 0.06	0.1 × 0.1 × 0.15	0.03 × 0.14 × 0.03
max θ collecd, deg	30	30	27
no. of indep reflcns	839	896	709
no. of reflcns used for the refinement	589 with $I \geq 2.0\sigma(I)$	683 with $I \geq 2.0\sigma(I)$	608 with $I \geq 2.0\sigma(I)$
final unweighted *R* factor	0.029	0.025	0.022
final weighted *R* factor	0.029	0.025	0.022
weighting scheme	$1/[\sigma(I)^2 + (0.03I)^2]^{1/2}$	$1/[\sigma(I)^2 + (0.03I)^2]^{1/2}$	$1/[\sigma(I)^2 + (0.03I)^2]^{1/2}$
extinction coeff, *g*	3.74×10^{-7}	1.22×10^{-6}	3.02×10^{-7}
max shift/error for non-hydrogen atoms	0.00	0.12	0.06
max shift/error for hydrogen atoms		0.35	0.37
final diff map highest peak, e/Å^3 (location)	1.67 (0.09, 0.97, 0.20)	0.98 (0, 0.25, −0.25)	1.13 (0.53, 0.23, 0.06)

(III): H, 2.05; N, 7.96; Cl 20.92.

For X-ray crystallography compound I was recrystallized from water as pale yellow crystals. II was recrystallized from 20% H_2O_2/80% H_2O. Recrystallization of II from H_2O alone at 80–100 °C gave compound III (on cooling over ca. 24 h).

Infrared spectra were recorded on a Perkin-Elmer spectrometer from 4000–250 cm^{-1} as KBr pellets. Major peaks are listed in Table I.

^{1}H-decoupled ^{195}Pt and ^{15}N NMR spectra were recorded on an XL-200 spectrometer at 300 K in 10-mm diameter sample tubes. Oxidation of ^{15}N-labeled *cis*-Pt$(NH_3)_2Cl_2$ with H_2O_2 was carried out in H_2O solution in the NMR tube using an external D_2O lock. Shifts are quoted to external Na_2PtCl_6 in D_2O and 2.9 M $^{15}NH_4Cl$ in 1 M HCl.

Crystal Structure Determinations

Crystal data, conditions for data collection and structure refinement, and the final *R* factors are summarized in Table II for each of the compounds. All the intensity data were measured with Mo Kα radiation on an Enraf-Nonius CAD4 automated diffractometer, operated in the θ–2θ scan mode. A periodic check on intensities of three strong reflections showed that no crystal decay occurred during each data collection. The crystal structures were solved by the heavy-atom method and refined by full-matrix least-squares procedures. The atomic scattering factors for the non-hydrogen and hydrogen atoms were taken from ref 7 and 8, respectively. Anomalous dispersion corrections from ref 7 were applied to platinum and chlorine atoms. Absorption correction was made by using a program written by Walker.[9] Corrections were made for extinction, and the coefficient was included in the refinement. In the case of comound I, attempts were made to locate hydrogen atoms that were not reported by Faggiani et al.;[5] however, they were not revealed clearly in a difference Fourier map. All the hydrogen atoms of compound II were revealed in a difference Fourier map calculated with all the non-hydrogen atoms

Table III. Atomic Coordinates with Estimated Standard Deviations

	x	*y*	*z*
	cis,cis,trans-PtCl$_2$(NH$_3$)$_2$(OH)$_2$ (I)		
Pt	0.2500	0.7500	0.02079 (3)
Cl	0.0258 (3)	0.7500 (4)	0.1642 (2)
O	0.252 (1)	0.4765 (8)	0.0255 (4)
N	0.045 (1)	0.750 (1)	−0.1021 (5)
	trans,trans,trans-PtCl$_2$(NH$_3$)$_2$(OH)$_2$ (II)		
Pt	0.0	0.0	0.0
Cl	0.3465 (3)	0.1600 (3)	0.1220 (2)
O	0.0546 (9)	0.0258 (6)	−0.2278 (8)
N	−0.1733 (8)	0.2614 (8)	−0.0321 (7)
H(1)	0.17 (1)	0.11 (1)	−0.221 (9)
H(2)	−0.128 (9)	0.34 (1)	0.073 (7)
H(3)	−0.12 (1)	0.34 (1)	−0.125 (9)
H(4)	−0.35	0.23	−0.07
	cis,trans,cis-PtCl$_2$(NH$_3$)$_2$(OH)$_2$ (III)		
Pt	0.20719 (6)	0.2500	0.23272 (6)
Cl(1)	0.3522 (4)	0.2500	−0.0872 (4)
Cl(2)	0.5302 (4)	0.2500	0.3927 (4)
O(1)	0.066 (1)	0.2500	0.502 (1)
O(2)	−0.071 (1)	0.2500	0.096 (1)
N	0.2054 (9)	0.5211 (8)	0.236 (1)
H(1)	0.17 (2)	0.25	0.57 (2)
H(2)	−0.17 (2)	0.25	0.20 (2)
H(3)	0.11 (1)	0.56 (1)	0.33 (1)
H(4)	0.33 (1)	0.57 (1)	0.23 (1)
H(5)	0.13 (1)	0.57 (1)	0.11 (2)

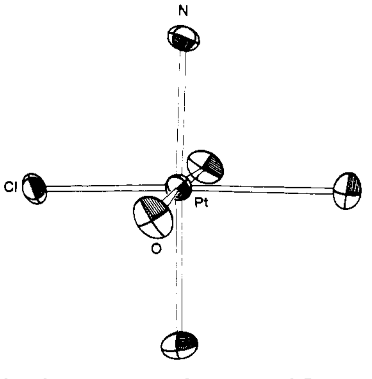

Figure 1. Molecular structure of compound I, *cis,cis,trans*-PtCl$_2$(NH$_3$)$_2$(OH)$_2$.

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(3) Laverick, M.; Nias, A. H. W.; Sadler, P. J.; Ismail, I. M. *Br. J. Cancer* **1981**, *43* (5), 732.
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Table IV. Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations

cis,cis,trans-$PtCl_2(NH_3)_2(OH)_2$ (I)			
Pt–Cl	2.317 (2)	Pt–N	2.056 (5)
Pt–O	2.008 (5)		
Cl–Pt–Cl′[a]	90.48 (8)	O–Pt–O′	176.9 (2)
Cl–Pt–O	89.2 (2)	O–Pt–N	91.3 (2)
Cl–Pt–O′	88.6 (2)	O–Pt–N′	90.8 (2)
Cl–Pt–N	87.6 (2)	N–Pt–N′	94.3 (3)
Cl–Pt–N′	178.1 (2)		
trans,trans,trans-$PtCl_2(NH_3)_2(OH)_2$ (II)			
Pt–Cl	2.303 (1)	N–H(2)	0.99 (6)
Pt–O	2.000 (5)	N–H(3)	1.07 (7)
Pt–N	2.038 (4)	N–H(4)	1.01 (5)
O–H(1)	0.89 (7)		
Cl–Pt–O	90.1 (1)	Pt–N–H(2)	112 (3)
Cl–Pt–N	90.3 (1)	Pt–N–H(3)	107 (4)
O–Pt–N	90.8 (2)	Pt–N–H(4)	108 (0)
Pt–O–H(1)	109 (4)		
cis,trans,cis-$PtCl_2(NH_3)_2(OH)_2$ (III)			
Pt–Cl(1)	2.325 (3)	O(1)–H(1)	0.8 (1)
Pt–Cl(2)	2.314 (3)	O(2)–H(2)	0.9 (1)
Pt–O(1)	2.010 (7)	N–H(3)	0.93 (8)
Pt–O(2)	1.992 (8)	N–H(4)	0.92 (9)
Pt–N	2.028 (6)	N–H(5)	1.0 (1)
Cl(1)–Pt–Cl(2)	92.7 (1)	O(1)–Pt–N	89.3 (2)
Cl(1)–Pt–O(1)	176.7 (2)	O(2)–Pt–N	90.0 (2)
Cl(1)–Pt–O(2)	87.5 (2)	N–Pt–N	178.6 (4)
Cl(1)–Pt–N	90.7 (2)	Pt–O(1)–H(1)	98 (8)
Cl(2)–Pt–O(1)	90.6 (2)	Pt–O(2)–H(2)	107 (8)
Cl(2)–Pt–O(2)	179.8 (2)	Pt–N–H(3)	108 (5)
Cl(2)–Pt–N	90.0 (2)	Pt–N–H(4)	113 (6)
O(1)–Pt–O(2)	89.2 (3)	Pt–N–H(5)	120 (6)

[a] Primed atoms are related to the corresponding unprimed atoms by a twofold axis of rotation.

as structure factor contributors ($R = 0.037$). The positional parameters of the H(4) did not refine well; hence, they were kept fixed during the refinement. For compound III, the systematic absences $0k0$ ($k = 2n$) specify that the possible space group assignments are either $P2_1$ or $P2_1/m$. The former was initially adopted, but the space group was later changed to $P2_1/m$ as the structure clearly showed a mirror plane perpendicular to the crystallographic b axis through the Pt atom. The structure refined well, including the positional and thermal parameters of hydrogen atoms. All the calculations were carried out on a PDP 11/34A computer using the SDP crystallographic program system unless otherwise stated. The atomic coordinates and bond lengths and angles are listed in Tables III and IV, respectively.

Results and Discussion

Our independent structure determination of compound I, the cis,cis,trans isomer is in good agreement with that of Faggiani et al.,[5] giving a closely octahedral coordination geometry for Pt(IV) (Figure 1). The compound has a crystallographic twofold symmetry, with the axis of symmetry bisecting Cl–Pt–Cl and N–Pt–N. We were able to monitor the formation of this compound by H_2O_2 oxidation of *cis*-$PtCl_2(^{15}NH_3)_2$ in an NMR tube. Only one product was observed with δ +860 (relative to external Na_2PtCl_6) and $^1J(^{195}Pt–^{15}N) = 275$ Hz in the ^{195}Pt NMR spectrum. The chemical shift and coupling constant are similar to those we have observed previously[10] for *cis,cis,trans*-$PtCl_2(i\text{-}PrNH_2)_2(OH)_2$ (J corrected for gyromagnetic ratio differences of ^{14}N and ^{15}N) and are indicative of a Pt(IV) complex with the nitrogen ligand trans to chloride.[11] Curiously the ^{15}N NMR spectrum (Figure 2) gave two sets of signals, the first (A) with δ −37.9 the major species (92% by integration—although NOE effects limit the accuracy of this) with $^1J(^{195}Pt–^{15}N) = 271$ Hz and the second (B) with δ −45.2 and $^1J(^{195}Pt–^{15}N) = 256$ Hz. The former resonance is attributed to compound I (that seen in the ^{195}Pt NMR spectrum), and the latter in view of its lower coupling constant is likely to have N trans to N rather than N trans to OH.[11] Two other very minor products can also be observed in the spectrum. It is notable that the ^{195}Pt satellites are of similar line widths as those of the main ^{15}N resonance, indicative of the negligible contribution of chemical shift anisotropy relaxation, as expected in octahedral Pt(IV) complexes that have higher symmetry than those of Pt(II).[10]

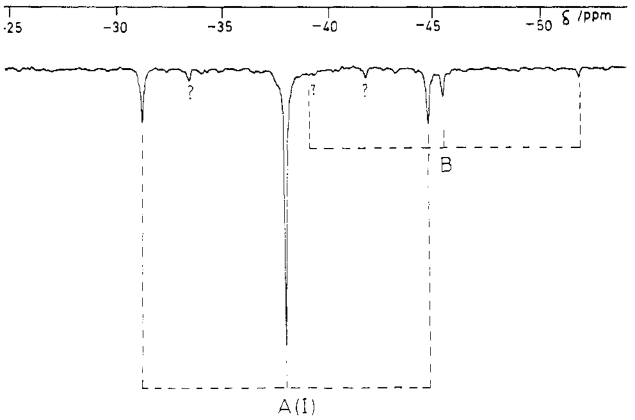

Figure 2. $^{15}N\{^1H\}$ NMR spectrum of *cis*-$PtCl_2(^{15}NH_3)_2$ in 20% H_2O_2/80% H_2O at 20.28 MHz showing the predominance of compound I as an approximate 1:4:1 triplet (pulsing conditions: scan width 10 kHz; transients 37 462; computer points 32 *k*; acquisition time 1.65 s; pulse width 7 μs (30°)).

For compound II, the space group $P2_1/c$ and the number of molecules in the unit cell require the molecule to reside on a center of inversion; therefore, the compound was proved to be the all-trans isomer.

There is a certain degree of ambiguity concerning the assignment of nitrogen and oxygen atoms as the scattering powers of the two atoms are similar. There are two possible assignments of isomers of compound III in the space group $P2_1/m$: *cis,cis,trans*-$PtCl_2(NH_3)_2(OH)_2$ and *cis,trans,cis*-$PtCl_2(NH_3)_2(OH)_2$, although the space group $P2_1$ extends the possibility to all-cis isomers as well. The assignment of *trans*-diammine was accepted on the following grounds:

(i) The R factors, prior to the allocation of hydrogen atoms, were 0.025 and 0.028 for the *trans*-diammine and *trans*-dihydroxo isomers, respectively.

(ii) The difference Fourier map based on non-hydrogen atoms showed three peaks with a geometry reasonable for a NH_3 group around the atoms in the trans position and only one peak around the atoms in the cis position, which again forms a reasonable geometry for an OH group. These hydrogen atoms refined well, and the final R factor was 0.022.

(iii) The weak hydrogen-bond network (discussed below) further confirms the position of the hydrogen atoms and therefore the assignment of atom types.

Compound III has a crystallographic mirror plane: hence, all the atoms except those of ammine groups lie in the mirror plane. The coordination octahedron of compound II is much more regular than that of I or III, due to the smaller repulsion between chloride atoms and between ammine groups (Table IV).

Hydrogen-bonding networks are observed in all three compounds (Table V). The hydrogen atoms of I were not located, but they seem to form weak hydrogen bonds between NH_3 and OH groups and between OH and Cl groups. In the all-trans

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(11) The assumption here is that the coupling constants in Pt(IV) complexes will be related to those of Pt(II), which are in the ranges 340–380, 290–320, and 280–290 Hz for OH, Cl, and $^{15}NH_3$ as ligands trans to $^{15}NH_3$. However, too few data are currently available on Pt(IV) complexes to test this.

Table V. Possible Hydrogen Bonds (A = Donor and B = Acceptor; Distances in Å and Angles in deg)

cis,cis,trans-$PtCl_2(NH_3)_2(OH)_2$ (I)

A-H···B	A···B	A-H···B	A···B
N-H···O[a]	2.87	O-H···Cl[b]	3.40

trans,trans,trans-$PtCl_2(NH_3)_2(OH)_2$ (II)

A-H···B	A-H	H···B	A···B	∠A-H···B
N-H(2)···O[c]	0.99	1.92	2.88	162
N-H(3)···O[d]	1.07	1.85	2.91	168
N-H(4)···Cl[e]	1.07	2.72	3.52	131
O-H(1)···Cl[d]	0.89	2.45	3.22	146

cis,trans,cis-$PtCl_2(NH_3)_2(OH)_2$ (III)

A-H···B	A-H	H···B	A···B	∠A-H···B
N-H(3)···O(1)[f]	0.9	2.14	3.01	156
N-H(5)···O(2)[f]	1.0	1.94	2.91	157
O(1)-H(1)···Cl(1)[g]	0.8	2.55	3.26	153
O(2)-H(2)···Cl(2)[h]	0.9	2.34	3.25	168

[a] $x - 1/2, y + 1/2, -z$. [b] $-x, -y + 1, -z$. [c] $x, 1/2 - y, 1/2 + z$. [d] $-x, 1/2 + y, -1/2 - z$. [e] $x - 1, y, z$. [f] $-x, -y + 1/2, -z + 1$. [g] $x, y, z + 1$. [h] $x - 1, y, z$.

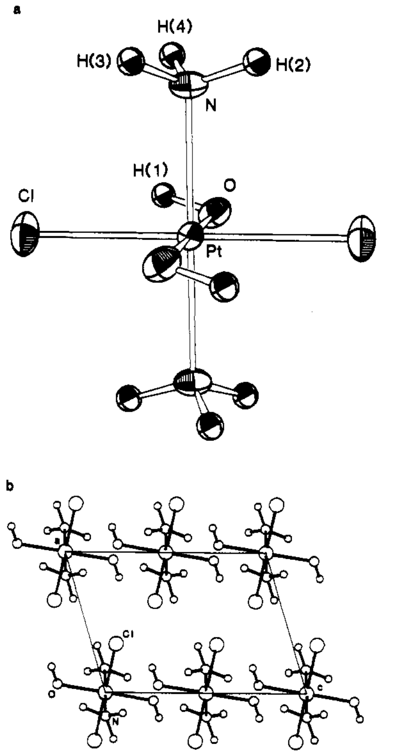

Figure 3. (a) Molecular structure and (b) *b*-axis projection of compound II, *trans,trans,trans*-$PtCl_2(NH_3)_2(OH)_2$.

isomer, II, all the hydrogen atoms are involved in a hydrogen-bond network. H(1), H(2), and H(3) atoms form hydrogen bonds between molecules related by the *c* glide planes and/or inversion center, and H(4) forms bonds between molecules related by translation along the *a* axis (Figure 3, Table V). In the *ac* plane of structure III, hydrogen bonds are found between the Cl and O atoms of adjacent molecules related by the unit cell translation. In the direction perpendicular to the *ac* plane, hydrogen bonds are formed between the ammine hydrogen atoms and the hydroxyl oxygen atoms (Figure 4, Table V).

During the structural study of II, a further batch of crystals was prepared by recrystallization from H_2O instead of dilute aqueous H_2O_2 solution. This procedure drastically changed the cell parameters, and it was proved by the current structure determination work that the all-trans isomer, II, had isomerized into the cis,trans,cis isomer, III.

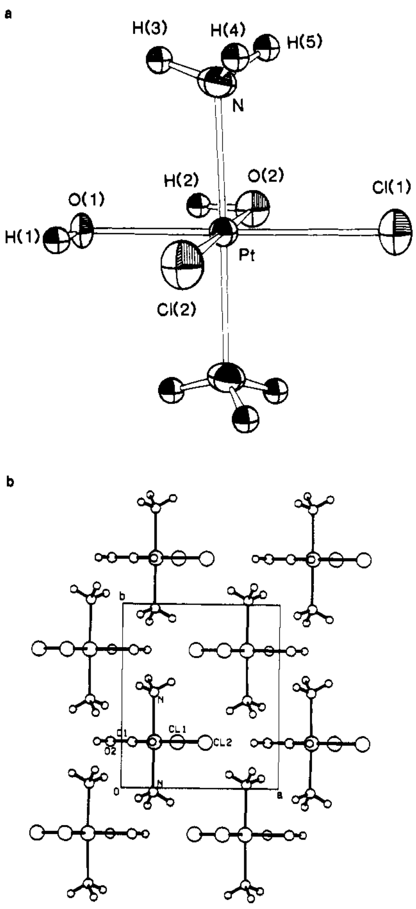

Figure 4. (a) Molecular structure and (b) *c*-axis projection of compound III, *cis,trans,cis*-$PtCl_2(NH_3)_2(OH)_2$.

We substantiated the finding by infrared studies (unfortunately we do not have ^{15}N-labeled samples of II and III for NMR studies). There are clear shifts of several peaks on conversion of II to III, for example $\nu(OH)$ from 3510 to 3460 cm^{-1}, $\nu(PtO)$ or $\nu(PtN)$ from 568 to 580 cm^{-1}, and the two $\nu(PtCl)$ bands at 350 and 325 cm^{-1} to one at 335 cm^{-1}. It also appears that isomerization is complete and that III is not a mixture of isomers. The infrared spectrum provides a clear distinction between all three isomers (Table I). Additionally quite a few crystals, after recrystallization of II from H_2O, were checked for cell parameters to confirm that we were not observing a minor conversion affecting a few crystals only.

The mechanism of the isomerization of this Pt(IV) complex requires further investigation. Since no isomerization is observed when H_2O_2 is present during recrystallization, it seems likely that a dissociation of OH^- or H_2O_2 is involved. Dissociation of H_2O_2 would give Pt(II), and substitution reactions of Pt(IV) complexes are commonly catalyzed by traces of Pt(II).[12] The conservation of the *trans*-diammine stereochemistry is perhaps a reflection of the greater bond strength of Pt–N vs. Pt–O and Pt–Cl. It has recently been observed that *cis*-dichlorobis(cycloheptylamino)platinum(II) isomerizes[13] on recrystallization from acetone.

The only other report of an isomerization of a Pt(IV) ammine complex appears to be that of Johnson and Widmer.[14] They found that *trans*-$Pt(NH_3)_4(OH)(SO_4)^+$ was converted into *cis*-$Pt(NH_3)_4(OH)_2^{2+}$ in the presence of added NaOH (pH 12–13). The reaction appeared to involve the neutral, deprotonated species $Pt(NH_3)_3(NH_2)(OH)(SO_4)$.

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Since much effort is currently devoted to antitumor testing of platinum diammines, it is clearly important for compounds to be well characterized by a wide range of physical techniques.

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Registry No. I, 31246-66-9; II, 31246-62-5; III, 31246-63-6.

Supplementary Material Available: Listings of the anisotropic thermal parameters of non-hydrogen atoms and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Reactions of Coordinated Ligands. 12.[1] Single-Stage Template Syntheses of Tetradentate Macrocyclic Phosphine Complexes

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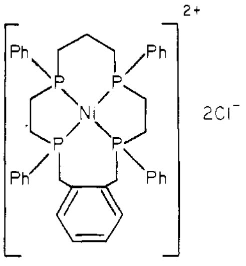
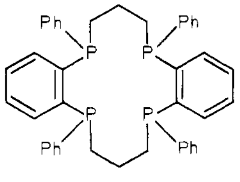
Square-planar complexes of nickel(II) and palladium(II) containing 14-membered macrocyclic tetradentate phosphine ligands are accessible by single-stage template-moderated ring-closure reactions between the complexes $[M(HMeP(CH_2)_nPMeH)_2]X_2$ (M = Ni, Pd; $n = 2, 3$; X = Cl, Br) and dialdehydes or diketones $RC(O)(CH_2)_nC(O)R$ ($n = 0, 1$; R = H, Me). For R = Me the formation of the macrocycles proceeds with high diastereoselectivity. The crystal and molecular structure of the two isomeric complexes **9a** and **9b** obtained by the reaction of acetylacetone and $[Pd(HMeP(CH_2)_2PMeH)_2]Cl_2$ shows the presence of a 14-membered ring system in both cases. Isomer **9a** crystallizes in the space group $C2/c$ with $a = 18.819$ (6) Å, $b = 11.607$ (2) Å, $c = 13.600$ (4) Å, $\beta = 90.81$ (4)°, $T = 21$ °C, $\lambda = 0.71069$ Å (Mo Kα), and $Z = 4$. The four phosphorus atoms display a square-planar coordination geometry at Pd(II) in the dication with the macrocyclic ring system in the trans-III (*RSSR*) arrangement. In isomer **9b**, in space group $P2_1$ with $a = 10.891$ (3) Å, $b = 15.766$ (6) Å, $c = 8.163$ (2) Å, $\beta = 108.4$ (2)°, $T = 21$ °C, $\lambda = 0.71069$ Å (Mo Kα), and $Z = 2$, the four phosphorus atoms and one chlorine atom form a square pyramid, the Pd atom being 0.26 Å above the basal plane. The configuration of the macrocyclic ring system may be assigned to the trans-I (*RSRS*) isomer.

Introduction

The first preparation of a macrocyclic ring system with four phosphorus atoms was carried out by Horner and co-workers,[2,3] who also proposed a template synthesis for ligands of this type or their complexes.[4] This synthetic method was, however, first successfully applied to phosphorus macrocycles by DelDonno and Rosen.[5] After a synthesis involving several steps, they were able to carry out the critical ring-closure reaction in the coordination sphere of nickel(II) to obtain complex I in low yield.



I



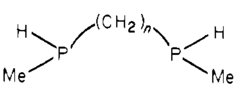
II

In 1977 Kyba, Hudson, McPhaul, and John described the synthesis of the macrocyclic, multidentate phosphine ligand II, which has two rigid *o*-phenylene bridges.[6] Of the five possible isomers (three meso and two *dl* pairs), one (cis-syn-cis) was investigated by X-ray structural analysis.[7]

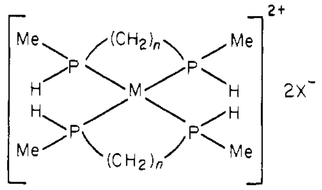
All syntheses of such ligands or of their complexes so far reported involve many reaction steps and give only poor yields.

The importance of macrocyclic multidentate phosphine ligands as phosphorus analogues of the crown ethers and the possible catalytic activity of their complexes make an easier access desirable.

In this paper we report a synthesis analogous to that for macrocyclic amines[8] and imines.[9] The multistep synthetic route is replaced by a template synthesis starting with suitable complexes of bidentate PH-functional phosphines, e.g.



1: $n = 2$
1a: $n = 3$



2: M = Ni, $n = 2$
3: M = Pd, $n = 2$
3a: M = Pd, $n = 3$

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