# Reactions of Planar Pentadentate Ligands with Palladium and Platinum Chlorides. Crystal Structures of *cis*-Dichlorobis(*N'*-isopropylidenebenzohydrazide)platinum(II) and the Cyclopalladated Dianion of *N'*,*N'''*-(Pyridine-2,6-diyldiethylidyne)bis(benzohydrazide) †

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The products from the reactions of the planar pentadentate ligand *N'*,*N'''*-(pyridine-2,6-diyldiethylidyne)bis(benzohydrazide) L$^1$, with $PdCl_4^{2-}$ and $PtCl_2$ have been investigated. In both cases extensive changes in the ligand L$^1$ occur so that square-planar complexes can be formed. With $PdCl_4^{2-}$, two cyclopalladation reactions take place involving the insertion of the Pd atom into a C–H and an N–H bond. The presence of an anionic nitrogen in a cyclopalladation product is unusual. The reaction of $PtCl_2$ in acetone with L$^1$ led to the displacement of the 2,6-diacetylpyridine group by acetone with the formation of the new ligand *N'*-isopropylidenebenzohydrazide, L$^2$, in the complex *cis*-$[PtCl_2(L^2)_2]$. Surprisingly, an analysis of the Pt–Cl and Pt–N distances in 23 *cis*- and 18 *trans*-$[PtCl_2L_2]$ (L = nitrogen donor ligand) complexes revealed no significant differences in the dimensions of the two geometries. The average Pt–Cl distances were 2.293(15) Å in the *cis* and 2.293(9) Å in the *trans* isomers.

The stereochemistry of Pd$^{II}$ and Pt$^{II}$ is dominated by four-co-ordinate square-planar complexes.[1] While examples of three-, five-, and six-co-ordinate complexes are known, these are exceptional. Complexes with unusual co-ordination numbers have been synthesized using planar pentadentate ligands,[2] prompting us to study the reactions of $PdCl_2$ and $PtCl_2$ with *N'*,*N'''*-(pyridine-2,6-diyldiethylidyne)bis(benzohydrazide) (L$^1$). Our results demonstrate that the planar pentadentate ligand L$^1$ is altered during the reaction so that a four-co-ordinate square-planar complex is the final product (Scheme). For Pd$^{II}$ an unusual example of a cyclopalladation reaction occurs. A new ligand is formed during the reaction with $PtCl_2$ by displacement of the 2,6-diacetylpyridine group. The extensive rearrangements which are observed indicate that the driving force for square-planar Pd$^{II}$ and Pt$^{II}$ is formidable.

## Results and Discussion

The $PdCl_4^{2-}$ ion in aqueous methanol at room temperature reacts with the ligand L$^1$ to give $[Pd(L^1 - 2H)]$ whose structure is shown in Figure 1. Two cyclopalladation reactions have occurred, and the final product contains adjacent five- and six-membered rings. A search of the Cambridge Structural Database[3] revealed only one compound containing a Pd–C bond and adjacent five- and six-membered rings.[4] The Pd–N(3) bond is unique in that N(3) is formally anionic. We have not found any other examples of cyclopalladation reactions involving an anionic nitrogen.[5,6]

A mechanism for *ortho*-cyclopalladation reactions has been proposed[7] which can be applied to the present case. The first step would involve the displacement of Cl$^-$ and co-ordination of the palladium to the pyridine nitrogen and one or both of the azomethine nitrogens. At this point an *ortho*-cyclopalladation reaction would give a six-membered or larger ring and the subsequent N–H insertion would yield the final product. Alternatively, the co-ordination of the pyridine nitrogen and one azomethine nitrogen could be followed by the N–H insertion and then the *ortho*-cyclopalladation. In either case the reaction could proceed without the formation of an intermediate with a high co-ordination number.

The pentadentate ligand L$^1$ is obviously no longer planar after the two insertion reactions. The C(11)O(2)N(6)C(14) plane is at an angle of 84.6° relative to the N(1)N(3)C(25)N(5) plane which moves O(2) out of the co-ordination sphere. However, the rotation also prevents delocalization along the C(9)N(5)N(6)C(11)C(14) chain. Consequently, the N(5)–N(6) distance of 1.418(11) Å is essentially a single bond and is significantly longer than the N(2)–N(3) bond of 1.350(11) Å (Table 1). Similarly, the C(11)–C(14) distance of 1.524(14) Å is significantly longer than the C(8)–C(24) distance of 1.467(14) Å. The distances in the approximately planar side chain C(6)N(2)N(3)C(8)C(24) are similar to those found in aromatic semicarbazones[8] or in the Co$^{II}$ and Ni$^{II}$ complexes with L$^1$.[2]

The Pd$^{II}$ atom is in the centre of an approximately square-planar arrangement formed by N(1), N(3), N(5), and C(25). The Pd–C bond lengths in a number of anionic ligands have been tabulated recently.[5] The 27 Pd–C($sp^2$) distances ranged from 1.922 to 2.204 Å, and the average of the 25 distances in the range 1.95—2.06 was 2.003(27) Å which is not significantly different from our value of 1.991(10) Å. The Pd–C($sp^2$) distance predicted from the appropriate radii is 1.97 Å. While the three nitrogen atoms are all $sp^2$ hybridized, the Pd–N(3) bond is unique since the N(3) atom is formally anionic. The Pd–N(3) distance of 1.942(8) Å is significantly shorter than the other two Pd–N distances of 2.045(8) Å to N(1) and 2.051(8) Å to N(5). The latter two Pd–N distances are surprisingly long compared to the Pd–C value since the N($sp^2$) radius is *ca.* 0.07 Å less than C($sp^2$). The anionic Pd–N(3) distance is more in line with the observed 'anionic' Pd–C distance. The conclusion is that the interaction with the formally negative atoms N(3) and C(24) is stronger than with the neutral nitrogen donors.

The reaction of $PtCl_2$ with L$^1$ in acetone produces the *cis*-dichlorobis(*N'*-isopropylidenebenzohydrazide)platinum(II) complex, $[PtCl_2(L^2)_2]$, whose structure is shown in Figure 2. Although acetone has been used as a solvent for the reaction of Schiff bases with metal ions without complications,[9] in this case displacement of the 2,6-diacetylpyridine has occurred to give the product. The steric constraints of the ligand prevent the

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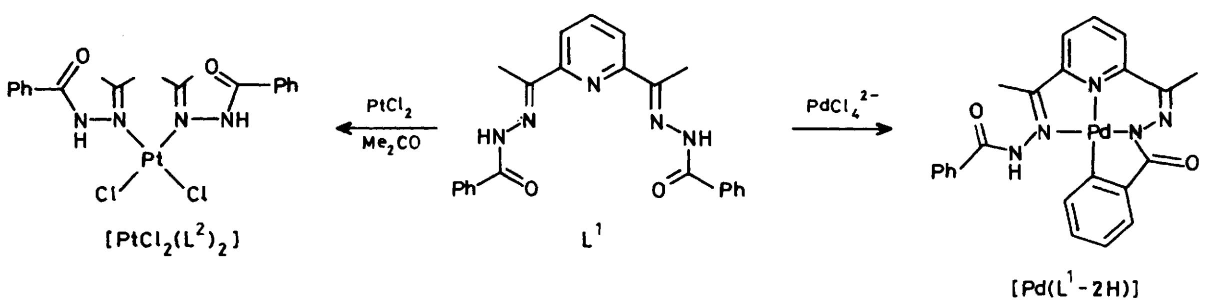
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



**Scheme.** L$^2$ = *N'*-Isopropylidenebenzohydrazide

**Table 1.** Bond distances (Å) and angles (°) involving the Pd atom in [Pd(L$^1$ − 2H)]·H$_2$O

| | | | |
|---|---|---|---|
| Pd–N(1) | 2.045(8) | Pd–C(25) | 1.991(10) |
| Pd–N(3) | 1.942(8) | Pd–N(5) | 2.051(8) |
| N(1)–C(1) | 1.343(12) | N(1)–C(5) | 1.308(13) |
| C(1)–C(2) | 1.415(16) | C(5)–C(4) | 1.406(17) |
| C(2)–C(3) | 1.348(16) | C(4)–C(3) | 1.384(16) |
| C(1)–C(6) | 1.450(15) | C(5)–C(9) | 1.468(14) |
| C(6)–C(7) | 1.506(14) | C(9)–C(10) | 1.506(15) |
| C(6)–N(2) | 1.298(14) | C(9)–N(5) | 1.286(15) |
| N(2)–N(3) | 1.350(11) | N(5)–N(6) | 1.418(11) |
| N(3)–C(8) | 1.390(14) | N(6)–C(11) | 1.351(14) |
| C(8)–O(1) | 1.231(12) | C(11)–O(2) | 1.210(15) |
| C(8)–C(24) | 1.467(14) | C(11)–C(14) | 1.524(14) |
| C(24)–C(25) | 1.393(15) | C(14)–C(15) | 1.347(19) |
| C(25)–C(26) | 1.391(14) | C(15)–C(16) | 1.396(19) |
| C(26)–C(27) | 1.393(17) | C(16)–C(17) | 1.355(18) |
| C(27)–C(28) | 1.350(18) | C(17)–C(18) | 1.343(20) |
| C(28)–C(29) | 1.370(16) | C(18)–C(19) | 1.391(16) |
| C(29)–C(24) | 1.392(17) | C(19)–C(14) | 1.373(16) |
| N(1)–Pd–N(3) | 92.8(3) | N(3)–Pd–N(5) | 171.2(3) |
| N(1)–Pd–N(5) | 78.6(3) | N(3)–Pd–C(25) | 81.8(4) |
| N(1)–Pd–C(25) | 174.3(4) | N(5)–Pd–C(25) | 106.8(4) |
| Pd–N(1)–C(1) | 121.6(7) | Pd–N(1)–C(5) | 114.2(6) |
| Pd–N(3)–N(2) | 128.3(6) | Pd–N(3)–C(8) | 118.4(6) |
| Pd–N(5)–N(6) | 128.1(6) | Pd–N(5)–C(9) | 115.7(7) |
| Pd–C(25)–C(24) | 112.4(7) | Pd–C(25)–C(26) | 130.2(8) |

**Table 2.** Bond distances (Å) and angles (°) involving the Pt atom in [PtCl$_2$(L$^2$)$_2$]

| | | | |
|---|---|---|---|
| Pt–Cl(1) | 2.289(2) | Pt–Cl(2) | 2.290(3) |
| Pt–N(11) | 2.039(8) | Pt–N(21) | 2.016(7) |
| N(11)–C(11) | 1.284(13) | N(21)–C(21) | 1.283(11) |
| C(11)–C(10) | 1.512(16) | C(21)–C(20) | 1.515(15) |
| C(11)–C(12) | 1.516(17) | C(21)–C(22) | 1.494(14) |
| N(11)–N(12) | 1.428(10) | N(21)–N(22) | 1.422(10) |
| N(12)–C(13) | 1.354(12) | N(22)–C(23) | 1.385(14) |
| C(13)–O(1) | 1.219(12) | C(23)–O(2) | 1.209(13) |
| C(13)–C(14) | 1.501(12) | C(23)–C(24) | 1.503(13) |
| C(14)–C(15) | 1.401(14) | C(24)–C(25) | 1.395(14) |
| C(15)–C(16) | 1.390(14) | C(25)–C(26) | 1.411(14) |
| C(16)–C(17) | 1.366(16) | C(26)–C(27) | 1.371(18) |
| C(17)–C(18) | 1.405(17) | C(27)–C(28) | 1.392(20) |
| C(18)–C(19) | 1.415(15) | C(28)–C(29) | 1.403(19) |
| C(19)–C(14) | 1.390(14) | C(29)–C(24) | 1.365(16) |
| Cl(1)–Pt–Cl(2) | 90.0(1) | N(11)–Pt–N(21) | 89.4(3) |
| Cl(1)–Pt–N(11) | 90.3(2) | Cl(2)–Pt–N(21) | 90.2(2) |
| Cl(1)–Pt–N(21) | 179.8(2) | Cl(2)–Pt–N(11) | 178.4(2) |
| Pt–N(11)–C(11) | 130.6(7) | Pt–N(21)–C(21) | 126.9(6) |
| Pt–N(11)–N(12) | 113.5(6) | Pt–N(21)–N(22) | 115.1(5) |

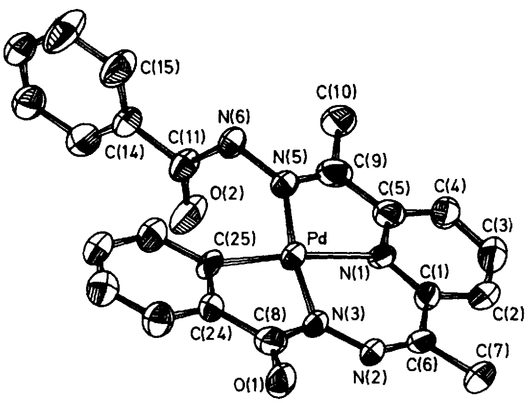


**Figure 1.** ORTEP drawing of [Pd(L$^1$ − 2H)] showing the atomic numbering and thermal ellipsoids

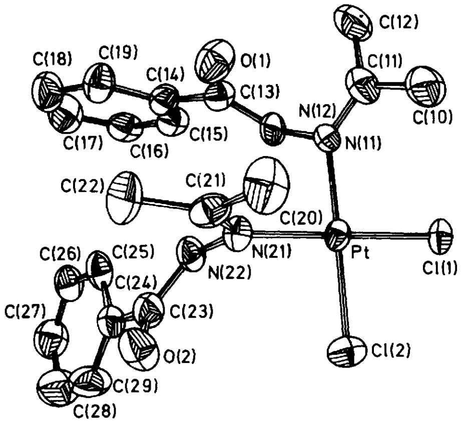


**Figure 2.** ORTEP drawing of *cis*-[PtCl$_2$(L$^2$)$_2$] showing the atomic numbering and thermal ellipsoids

PtCl$_2$N$_2$ fragment from being planar. However, the maximum deviations of 0.046 Å are small.

The co-ordinated L$^2$ ligand is not planar as would be expected in the absence of steric effects. The two C=O groups are twisted slightly (17.1 and 26.7°) from the plane of the attached phenyl group. The Me$_2$C=N groups form angles of 75.3 and 65.6° with the corresponding CC=ON groups. The large deviations from planarity are required if two ligands are to co-ordinate to the same Pt atom in a *cis* arrangement. The differences in the bond lengths of the two ligands are not significant. The average distances in the ligand side chain (C=N 1.283, N–N 1.425, N–C 1.370, C=O 1.214, C–C 1.502 Å)

**Table 3.** A comparison of the Pt–Cl and Pt–N distances (Å) in *cis*- and *trans*-$[PtCl_2L_2]$ complexes where L is an N donor

(*a*) *cis*-$[PtCl_2L_2]$ complexes

| | Ref. | *R*[a] | Pt–Cl | | Pt–N | | Hybridization[b] |
|---|---|---|---|---|---|---|---|
| $[PtCl_2(HNCH_2CH_2)_2]$ | 10 | 0.083 | 2.295 | 2.298 | 2.025 | 1.848[c] | $sp^3$ |
| $[PtCl_2\{MeNHCH_2CH(Me)NH_2\}]$ | 11 | 0.035 | 2.307 | 2.298 | 2.013 | 2.028 | $sp^3$ |
| $[\{PtCl_2[H_2NCHCH(NH_2)CH_2CH_2CH_2]\}_3]$ | 12 | 0.059 | 2.291 | 2.286 | 2.026 | 2.061 | $sp^3$ |
| | | | 2.291 | 2.283 | 2.042 | 2.014 | |
| | | | 2.291 | 2.286 | 2.026 | 2.061 | |
| $[PtCl_2(H_2NCHCH_2CH_2)_2]$ | 13 | 0.055 | 2.287 | 2.271 | 2.048 | 2.041 | $sp^3$ |
| $[PtCl_2\{H_2NCH(CH_2)_2CH_2\}_2]$ | 14 | 0.046 | 2.326 | 2.316 | 2.057 | 2.062 | $sp^3$ |
| $[PtCl_2\{H_2NCH(CH_2)_4CH_2\}_2]$ | 15 | 0.054 | 2.308 | *d* | 2.127[c] | *d* | $sp^3$ |
| $[PtCl_2\{H_2NCH(CH_2)_4CH_2\}_2]\cdot P(O)(NMe_2)_3$ | 16 | 0.055 | 2.305 | 2.325 | 2.061 | 2.049 | $sp^3$ |
| $[PtCl_2(NH_3)_2]\cdot Me_2NCHO$ | 17 | 0.039 | 2.315 | 2.307 | 2.002 | 2.083 | $sp^3$ |
| $[PtCl_2\{H_2NCH_2C(O)NHCH_2CO_2Et\}_2]$ | 18 | 0.039 | 2.297 | 2.315 | 2.046 | 2.039 | $sp^3$ |
| $[PtCl_2(H_2NCH_2CO_2H)_2]$ | 19 | 0.133 | 2.301 | 2.276 | 2.079 | 2.091 | $sp^3$ |
| $[PtCl_2(py)(H_2NCH_2CO_2H)]$ (triclinic)[e] | 20 | 0.108 | 2.306 | 2.297 | 1.968[c] | 1.931[c] | $sp^3/sp^2$ |
| $[PtCl_2(py)(H_2NCH_2CO_2H)]$ (monoclinic)[e] | 21 | 0.086 | 2.298 | 2.295 | 2.043 | 2.041 | $sp^3/sp^2$ |
| $[PtCl_2(py)_2]$[e] | 22 | 0.041 | 2.290 | 2.300 | 2.007 | 2.038 | $sp^2$ |
| $[PtCl_2(bipy)]$[f] | 23 | 0.024 | 2.328[c] | *d* | 2.001 | *d* | $sp^2$ |
| $[PtCl_2(caf)_2]$[g] | 24 | 0.025 | 2.271 | *d* | 2.030 | *d* | $sp^2$ |
| $[PtCl_2(mim)]$[h] | 25 | 0.046 | 2.297 | *d* | 2.015 | *d* | $sp^2$ |
| $[PtCl_2(hemnim)_2]$[i] | 26 | 0.074 | 2.287 | 2.286 | 2.026 | 2.022 | $sp^2$ |
| $[PtCl_2\{Me_2CNNHC(O)Ph\}_2]$ | *j* | 0.038 | 2.289 | 2.290 | 2.039 | 2.016 | $sp^2$ |
| $[PtCl_2(Me_8P_4N_4)]$ | 27 | 0.048 | 2.331[c] | 2.391[c] | 2.027 | 2.018 | $sp^2$ |
| $[PtCl_2\{(MeNH)_8P_4N_4\}]$ | 28 | 0.049 | 2.302 | 2.299 | 2.026 | 2.082[c] | $sp^2$ |
| $[PtCl_2(NCPh)_2]$ | 29 | 0.059 | 2.268 | 2.293 | 2.013 | 1.978 | $sp$ |
| $[PtCl_2(NCMe)_2]$ | 30 | 0.053 | 2.264 | 2.263 | 1.978 | 1.980 | $sp$ |
| $[PtCl_2(NCMe)_2]$ | 30 | 0.057 | 2.270 | 2.277 | 1.945 | 1.986 | $sp$ |
| Average for $sp^3$ donors | | | 2.298(14) | | 2.045(23) | | |
| Average for $sp^2$ donors | | | 2.293(9) | | 2.023(12) | | |
| Average for $sp$ donors | | | 2.272(10) | | 1.980(20) | | |
| Average for all donors | | | 2.293(15) | | 2.029(30) | | |

(*b*) *trans*-$[PtCl_2L_2]$ complexes

| | Ref. | *R*[a] | Pt–Cl | | Pt–N | | Hybridization[b] |
|---|---|---|---|---|---|---|---|
| $[PtCl_2(HNCH_2CH_2)_2]$ | 10 | 0.065 | 2.297 | *d* | 2.044 | *d* | $sp^3$ |
| $[PtCl_2(H_2NCHCH_2CH_2)_2]$ | 14 | 0.027 | 2.298 | *d* | 2.047 | *d* | $sp^3$ |
| $[PtCl_2\{H_2NCH(CH_2)_4CH_2\}_2]$ | 31 | 0.041 | 2.302 | *d* | 2.078 | *d* | $sp^3$ |
| $[PtCl_2\{H_2NCH(CH_2)_5CH_2\}_2]$ | 32 | 0.029 | 2.296 | *d* | 2.065 | *d* | $sp^3$ |
| | 32 | 0.029 | 2.303 | *d* | 2.061 | *d* | $sp^3$ |
| $[PtCl_2(Me_3CONH_2)_2]$ | 33 | 0.107 | 2.290 | 2.281 | 2.117[c] | 2.053 | $sp^3$ |
| $[PtCl_2\{PhCH_2CH(NH_2)CO_2Et\}_2]$ | 34 | 0.057 | 2.285 | 2.311 | 2.085 | 2.066 | $sp^3$ |
| $[PtCl_2\{EtO_2CCH_2CH(NH_2)CO_2Et\}_2]$ | 35 | 0.039 | 2.278 | 2.253[c] | 2.066 | 2.060 | $sp^3$ |
| | 35 | 0.039 | 2.280 | 2.271 | 2.120[c] | 2.082 | $sp^3$ |
| $[PtCl_2(NH_3)(H_2NCH_2CO_2H)]$ | 36 | 0.110 | 2.290 | 2.294 | 2.018 | 2.029 | $sp^3$ |
| $[PtCl_2(NH_3)(Me\text{-}cyt)]$[k] | 37 | 0.061 | 2.288 | 2.296 | 2.044 | 2.030 | $sp^3/sp^2$ |
| $[PtCl_2(NH_3)(pro)]$[l] | 38 | 0.096 | 2.329[c] | 2.289 | 2.178[c] | 2.105 | $sp^3/sp^2$ |
| $[PtCl_2(pym)_2]$[m] | 39 | 0.029 | 2.296 | *d* | 2.008 | *d* | $sp^2$ |
| $[PtCl_2(py)_2]$[e] | 22 | 0.068 | 2.308 | *d* | 1.977 | *d* | $sp^2$ |
| $[PtCl_2(ecpy)]$[n] | 40 | 0.055 | 2.297 | *d* | 1.991 | *d* | $sp^2$ |
| $[PtCl_2(hemnim)_2]$[i] | 26 | 0.046 | 2.296 | *d* | 2.000 | *d* | $sp^2$ |
| $[PtCl_2(mhpnim)_2]$[o] | 41 | 0.037 | 2.294 | *d* | 2.014 | *d* | $sp^2$ |
| $[PtCl_2(Bu^tNO)_2]$ | 42 | 0.029 | 2.295 | *d* | 1.967 | *d* | $sp^2$ |
| $[PtCl_2(NCPh)_2]$ | 29 | 0.056 | 2.292 | *d* | 1.978 | *d* | $sp$ |
| $[PtCl_2(NCPh)_2]$ | 43 | 0.029 | 2.265[c] | *d* | 1.950 | *d* | $sp$ |
| Average for $sp^3$ donors | | | 2.291(10) | | 2.057(19) | | |
| Average for $sp^2$ donors | | | 2.295(5) | | 2.012(40) | | |
| Average for $sp$ donors | | | | | 1.964(14) | | |
| Average for all donors | | | 2.293(9) | | 2.034(40) | | |

[a] Crystallographic *R* index. [b] Hybridization of donor N atom. [c] Value not included in the calculation of the average values. [d] Determined by symmetry. [e] py = Pyridine. [f] bipy = 2,2′-Bipyridine. [g] caf = Caffeine. [h] mim = *N*-Methylimidazole. [i] hemnim = 1-(2′-Hydroxyethyl)-2-methyl-5-nitroimidazole-$N^3$. [j] This work. [k] Me-cyt = 1-Methylcytosine-$N^3$. [l] pro = L-Proline. [m] pym = Pyrimidine. [n] ecpy = 4-Ethoxycarbonylpyridine. [o] mhpnim = 1-(2′-hydroxy-3′-methoxypropyl)-2-nitroimidazole-$N^3$.

are reasonable values for a non-delocalized hydrazone group (Table 2). These values are essentially the same as those observed in the twisted side chain of the $[Pd(L^1 - 2H)]$ complex.

A search of the 1986 release of the Cambridge Crystallographic Data Centre file located 23 *cis*- and 18 *trans*-$[PtCl_2L_2]$ structures, where L is a nitrogen donor. These data are summarized in Table 3. The data for each isomer are arranged in

**Table 4.** Final atomic co-ordinates ( × $10^4$) for the non-hydrogen atoms in $[Pd(L^1 - 2H)]\cdot H_2O$

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Pd | 2 178(1) | 4 929(1) | 1 071(1) | C(8) | 1 061(14) | 7 398(10) | 1 052(8) |
| O(1) | 599(11) | 8 449(6) | 702(6) | C(9) | 3 144(15) | 2 509(10) | 739(9) |
| O(2) | 5 132(10) | 3 215(9) | 3 568(7) | C(10) | 3 530(16) | 1 139(10) | 842(10) |
| O(W1) | −163(12) | 559(7) | 1 633(6) | C(11) | 3 889(14) | 2 528(10) | 3 483(9) |
| N(1) | 2 764(10) | 4 437(7) | −339(6) | C(14) | 3 688(14) | 1 775(9) | 4 532(8) |
| N(2) | 1 650(12) | 7 105(7) | −610(6) | C(15) | 2 290(17) | 1 087(14) | 4 525(10) |
| N(3) | 1 668(12) | 6 615(7) | 440(6) | C(16) | 2 241(16) | 401(15) | 5 523(11) |
| N(5) | 2 715(12) | 3 083(7) | 1 487(7) | C(17) | 3 577(16) | 466(11) | 6 514(9) |
| N(6) | 2 607(12) | 2 347(8) | 2 467(7) | C(18) | 4 968(17) | 1 157(11) | 6 522(9) |
| C(1) | 2 676(14) | 5 248(10) | −1 236(8) | C(19) | 5 053(16) | 1 823(11) | 5 527(10) |
| C(2) | 3 264(14) | 4 836(10) | −2 097(9) | C(24) | 1 079(16) | 6 789(10) | 2 165(8) |
| C(3) | 3 782(17) | 3 671(11) | −2 053(9) | C(25) | 1 641(13) | 5 588(9) | 2 398(8) |
| C(4) | 3 763(17) | 2 843(10) | −1 141(10) | C(26) | 1 757(16) | 5 045(10) | 3 484(9) |
| C(5) | 3 181(14) | 3 274(9) | −292(8) | C(27) | 1 306(16) | 5 676(11) | 4 296(9) |
| C(6) | 2 145(14) | 6 515(9) | −1 325(8) | C(28) | 717(18) | 6 818(12) | 4 016(10) |
| C(7) | 1 981(17) | 7 224(11) | −2 456(9) | C(29) | 595(15) | 7 407(11) | 2 966(9) |

**Table 5.** Final atomic co-ordinates ( × $10^5$ for Pt, × $10^4$ for other atoms) in $[PtCl_2(L^2)_2]$

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Pt | 6 978(4) | 45 789(3) | 17 667(3) | C(16) | 1 759(11) | 10 226(9) | 1 553(11) |
| Cl(1) | 815(3) | 2 937(2) | 147(2) | C(17) | 1 949(13) | 11 092(9) | 2 673(12) |
| Cl(2) | −1 476(3) | 3 893(2) | 1 612(3) | C(18) | 2 575(13) | 10 785(10) | 3 866(12) |
| O(1) | 3 898(8) | 7 087(6) | 3 859(7) | C(19) | 3 018(12) | 9 548(9) | 3 910(10) |
| O(2) | −1 788(8) | 7 088(6) | 3 823(7) | C(20) | 2 054(13) | 5 016(10) | 4 850(10) |
| N(11) | 2 603(7) | 5 226(6) | 1 878(7) | C(21) | 1 259(10) | 6 134(9) | 4 396(9) |
| N(12) | 2 525(8) | 6 481(6) | 1 770(7) | C(22) | 1 347(14) | 7 300(10) | 5 402(10) |
| N(21) | 601(7) | 6 028(6) | 3 193(6) | C(23) | −1 387(11) | 7 496(8) | 3 120(9) |
| N(22) | −181(8) | 7 075(6) | 2 791(7) | C(24) | −2 112(10) | 8 578(8) | 2 575(9) |
| C(10) | 4 067(12) | 3 426(10) | 2 332(14) | C(25) | −1 322(11) | 9 366(8) | 2 293(9) |
| C(11) | 3 843(10) | 4 697(9) | 2 048(11) | C(26) | −2 023(12) | 10 383(9) | 1 795(10) |
| C(12) | 5 083(12) | 5 277(11) | 1 909(14) | C(27) | −3 467(13) | 10 582(10) | 1 583(12) |
| C(13) | 3 133(10) | 7 346(8) | 2 859(9) | C(28) | −4 241(14) | 9 812(12) | 1 898(16) |
| C(14) | 2 765(9) | 8 663(8) | 2 764(9) | C(29) | −3 536(11) | 8 811(10) | 2 409(13) |
| C(15) | 2 167(10) | 9 005(8) | 1 590(10) | | | | |

terms of the hybridization of the donor nitrogen atom. Within the same hybridization, chemically similar donors are grouped together. The average Pt–Cl and Pt–N bond lengths are also given for each isomer and hybridization. Individual values which were more than 3σ from the average value were not included in the calculations and are identified in Table 3.

For both isomers, the Pt–N distances show the expected correlation with a change in the N hybridization. Unfortunately, the e.s.d. of the average value is high so that the differences are not significant. The average Pt–N distances are not significantly different.

Surprisingly, the Pt–Cl distances in both the *cis* and *trans* isomers show no significant variation with the nature of the nitrogen donor. An unexpected observation is the similarity between the average Pt–Cl distances in *cis* and *trans* isomers. The average of the 67 Pt–Cl distances used in the calculations was 2.293(13) Å. This equality of the Pt–Cl bond distance in both isomers is important in developing a mechanism for the antitumour activity of various *cis*-$[PtCl_2L_2]$ complexes *versus* the generally inactive *trans* isomer. Assuming that the bond distance is related to the ease of bond breaking, there appears to be no structural rationale for a difference in the reaction rates of the two isomers.

## Experimental

*Materials.*—The synthesis of $L^1$ has been reported previously.[2] All solvents and chemicals were reagent grade and were used as supplied.

*Preparation of* $[Pd(L^1 - 2H)]\cdot H_2O$.—Sodium chloride (0.468 g, 8.0 mmol) and $PdCl_2$ (0.1773 g, 1.0 mmol) were dissolved in water (30 $cm^3$). This solution was slowly added to a solution of $L^1$ (0.3990 g, 1.0 mmol) in MeOH (60 $cm^3$). A small amount of yellow solid was formed which was filtered off. On standing, orange crystals of the product appeared. Crystals suitable for diffraction studies were grown from MeOH (Found: C, 52.9; H, 4.0; Cl, 0.0; N, 13.4. Calc. for $C_{23}H_{21}N_5O_3Pd$: C, 52.9; H, 4.1; Cl, 0.0; N, 13.4%).

*Crystal Data.*—$C_{23}H_{21}N_5O_3Pd$, $M = 521.9$, triclinic, $a = 8.839(4)$, $b = 10.461(4)$, $c = 12.101(5)$ Å, $\alpha = 88.14(3)$, $\beta = 110.35(3)$, $\gamma = 97.20(3)^\circ$, $U = 1\,040.7(8)$ Å$^3$, space group $P\bar{1}$, $Z = 2$, $D_c = 1.665$, $D_m = 1.71$ g $cm^{-3}$, $F(000) = 528$, $\mu = 9.1$ $cm^{-1}$. Crystal dimensions 0.05 × 0.09 × 0.43 mm.

*Preparation of* $[PtCl_2(L^2)_2]$.—A suspension of $L^1$ (0.399 g, 1.0 mmol) and $PtCl_2$ (0.266 g, 1.0 mmol) in acetone was refluxed for 48 h. The solution was filtered and cooled. Yellow crystals formed on evaporation of the solvent (Found: C, 39.3; H, 4.0; Cl, 11.1; N, 8.9. Calc. for $C_{20}H_{24}Cl_2N_4O_2Pt$: C, 38.8; H, 3.9; Cl, 11.5; N, 9.1%).

*Crystal Data.*—$C_{20}H_{24}Cl_2N_4O_2Pt$, $M = 618.43$, triclinic, $a = 9.924(4)$, $b = 11.153(5)$, $c = 11.489(5)$ Å, $\alpha = 104.48(3)$, $\beta = 110.73(3)$, $\gamma = 84.53(3)^\circ$, $U = 1\,151.5(8)$ Å$^3$, space group $P\bar{1}$, $Z = 2$, $D_c = 1.784$, $D_m = 1.89$ g $cm^{-3}$, $F(000) = 600$, $\mu = 64.1$ $cm^{-1}$. Crystal dimensions 0.15 × 0.09 × 0.05 mm.

*Data Collection and Processing.*—All measurements were made using a Nicolet $P\bar{1}$ diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.710 69 Å). The cell dimensions were determined by a least-squares refinement of 15 automatically centred reflections. A variable-speed (1—24° min$^{-1}$) $\theta$—$2\theta$ scan technique was used to measure the intensity data from 0 to 45° in $2\theta$. Four standard reflections were measured after every 96 reflections and were used to correct for small variations ($\pm 4\%$ in each case) during data collection. 2 472 Reflections for the Pd complex and 3 513 reflections for the Pt complex with $I \geqslant 2\sigma(I)$ were used in the analysis. No absorption corrections were made.

*Structure Analysis and Refinement.*—The intensity statistics indicated $P\bar{1}$ as the space group and both structures were solved and refined in that space group. Normal heavy-atom procedures were used (Patterson and Fourier syntheses) followed by least-squares refinement. Full-matrix refinement was used with individual isotropic thermal parameters followed by blocked least-squares refinement with anisotropic thermal parameters. The weights in the least-squares refinement were $w = 1/[\sigma(F)]^2$. A difference Fourier synthesis was used to locate the hydrogen atoms in both complexes. In $[Pd(L^1 - 2H)]$ the hydrogen atom positions were refined, giving some improvement in the distances and angles involving these atoms. However, the reduction in $R$ to 0.081 and $R'$ to 0.056 was not significant. The difference between $R$ and $R'$ suggests that the $2\sigma$ cut-off for observed intensities may have been too low. Least-squares refinement with the H atoms included did not give any significant reduction in the final values of $R$ of 0.036 and $R'$ of 0.038 for $[PtCl_2(L_2)_2]$. All computer programs were written by G. J. P. except for ORTEP which was adapted for our local programs and computer. The final positional parameters are given in Tables 4 and 5. The final bond distances involving the non-hydrogen atoms and bond angles around the metal ion are listed in Tables 1 and 2.

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