Preparation, Crystal Structure and Attempts to Cyclometallate *trans*-Bis(D-camphor oxime-*N*)dichloropalladium(II) ‡

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The title complex was prepared and shown to be resistant towards cyclometallation, as were the corresponding dibromo- and di-iodo-complexes. Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, with a = 1 263.1(3), b = 2 610.5(10), c = 685.3(2) pm, and Z = 4. The molecule has approximate C_2 symmetry, with both camphoryl groups to the same side of the co-ordination plane, while the two oxime O–H groups on the other side engage in an unusual hydrogen-bond chelate system with a chlorine atom of a neighbouring molecule.

It has been established that steric effects, *e.g.* steric compression, can promote cyclometallation reactions such as cyclopalladation.[1–3] With this in mind we hoped to be able to palladate the sterically hindered but readily available oxime, D-camphor oxime (D-camo) which then might be useful in synthesis. We have shown that the sterically hindered t-butyl methyl ketoxime is readily cyclopalladated on the t-butyl group.[4] Treatment of $Na_2[PdCl_4]$ with D-camphor oxime readily gave *trans*-$[PdCl_2(\text{D-camo})_2]$ in high yield (preparative details and characterising data are in the Experimental section). However, this compound resisted all attempts to effect cyclometallation such as heating in high-boiling solvents (chlorobenzene or 1,1,2,2-tetrachloroethane) or heating with sodium acetate in ethanol or acetone. Usually, *trans*-$[PdCl_2(\text{D-camo})_2]$ was recovered essentially unchanged. Since metal bromides or iodides often cyclometallate more readily than chlorides,[5] we have treated *trans*-$[PdCl_2(\text{D-camo})_2]$ with lithium bromide or sodium iodide in acetone to give *trans*-$[PdBr_2(\text{D-camo})_2]$ or *trans*-$[PdI_2(\text{D-camo})_2]$, respectively. Preparative details and characterising data for these complexes are given in the Experimental section. These two complexes were also resistant to cyclometallation when treated with sodium acetate in ethanol or on heating in high-boiling solvents (chlorobenzene, *etc.*).

In order to look for reasons why *trans*-$[PdCl_2(\text{D-camo})_2]$ was so resistant to cyclopalladation its structure was determined by *X*-ray diffraction.

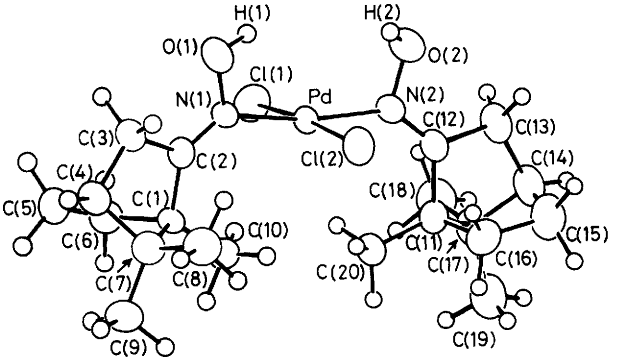

Figure 1. ORTEP drawing showing the molecular structure and atom numbering

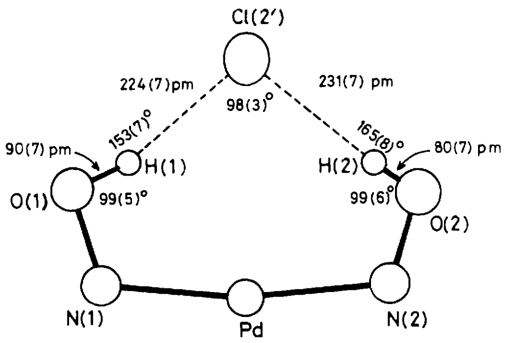

Figure 2. The intermolecular hydrogen bonding, showing distances and angles, with estimated standard deviations in parentheses. The distances O(1) ··· Cl(2′) and O(2) ··· Cl(2′) are 306.5(4) and 308.4(5) pm respectively

The molecular structure and atom numbering are shown in Figure 1; bond lengths and some bond angles are given in Table 1. The molecule is seen to have approximate C_2 symmetry with both camphoryl groups to one side of the palladium-atom co-ordination plane and both OH groups on the other side. The approach of the C(10) and C(20) hydrogen atoms to palladium (288, 313, 289, and 302 pm) would be much closer were it not for the very large Pd–N(1)–C(2) and Pd–N(2)–C(12) angles of 136.7(4) and 135.9(4)° respectively. The distances Pd–C(10) and Pd–C(20) are both 333 pm. On the other side of the co-ordination plane the two oxime hydrogen atoms form an interesting hydrogen-bond chelate system with Cl(2) of a neighbouring molecule, to give the eight-membered ring shown in Figure 2. These hydrogen bonds link the molecules into chains running in the z direction. The fact that Cl(2) engages in two hydrogen bonds while Cl(1) forms none is reflected in the Pd–Cl(1) and Pd–Cl(2) bond lengths of 228.0(1) and 230.7(1) pm respectively.

Thus the geometry of the molecule is such that the carbon atoms C(10) or C(20) are not forced into the vicinity of the palladium and the palladium–chlorine bonds are orthogonal to the approximate planes defined by Pd–N(1)–C(2)–C(1)–C(10) and by Pd–N(2)–C(12)–C(11)–C(20). In other systems in which cyclometallation occurs readily the chlorine to be displaced is often held in close proximity to the carbon (or oxygen) which is to be metallated and which will take up the vacated co-ordination site.[6,7] Thus steric factors in $[PdCl_2(\text{D-camo})_2]$ are not acting in a manner which would promote cyclometallation.

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Table 1. Bond lengths (pm) and selected angles (°) with estimated standard deviations in parentheses

Pd–Cl(1)	228.0(1)	Pd–Cl(2)	230.7(1)	C(2)–C(3)	151.4(7)	C(12)–C(13)	152.2(7)
Pd–N(1)	202.3(4)	Pd–N(2)	202.6(4)	C(3)–C(4)	154.1(7)	C(13)–C(14)	153.1(9)
N(1)–C(2)	127.6(6)	N(2)–C(12)	127.2(6)	C(4)–C(5)	153.7(8)	C(14)–C(15)	150.7(11)
N(1)–O(1)	140.6(5)	N(2)–O(2)	140.4(6)	C(4)–C(7)	156.1(7)	C(14)–C(17)	155.1(8)
C(1)–C(2)	150.0(6)	C(11)–C(12)	150.2(7)	C(5)–C(6)	152.7(7)	C(15)–C(16)	156.3(9)
C(1)–C(6)	156.5(7)	C(11)–C(16)	155.9(8)	C(7)–C(8)	152.9(7)	C(17)–C(18)	152.1(10)
C(1)–C(7)	157.0(7)	C(11)–C(17)	157.0(7)	C(7)–C(9)	152.8(7)	C(17)–C(19)	153.7(8)
C(1)–C(10)	150.3(6)	C(11)–C(20)	151.0(6)	O(1)–H(1)	90(7)	O(2)–H(2)	80(7)
Cl(1)–Pd–Cl(2)	175.0(1)	N(1)–Pd–N(2)	169.7(2)	Pd–N(1)–O(1)	111.5(3)	Pd–N(2)–O(2)	112.1(3)
Cl(1)–Pd–N(1)	91.3(1)	Cl(1)–Pd–N(2)	90.9(1)	Pd–N(1)–C(2)	136.7(4)	Pd–N(2)–C(12)	135.9(4)
Cl(2)–Pd–N(1)	88.5(1)	Cl(2)–Pd–N(2)	90.2(1)	O(1)–N(1)–C(2)	111.2(4)	O(2)–N(2)–C(12)	111.8(4)

Table 2. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd	0.087 29(3)	0.023 74(1)	0.202 46(6)
Cl(1)	−0.021 74(11)	0.039 59(6)	0.460 74(21)
Cl(2)	0.184 78(10)	0.008 53(5)	−0.076 31(21)
N(1)	0.052 9(2)	−0.051 9(1)	0.212 0(6)
N(2)	0.146 3(2)	0.095 8(1)	0.216 8(6)
O(1)	0.132 9(2)	−0.079 7(1)	0.307 5(6)
O(2)	0.227 0(2)	0.100 2(2)	0.356 7(6)
H(1)	0.167 8(57)	−0.053 4(28)	0.364 0(121)
H(2)	0.250 1(56)	0.071 9(24)	0.351 7(123)
C(1)	−0.114 2(2)	−0.068 0(2)	0.026 0(6)
C(2)	−0.015 1(3)	−0.081 8(2)	0.134 6(6)
C(3)	−0.006 9(4)	−0.139 6(2)	0.142 1(8)
C(4)	−0.106 0(3)	−0.155 2(2)	0.025 3(7)
C(5)	−0.201 7(4)	−0.144 4(2)	0.157 5(9)
C(6)	−0.204 6(3)	−0.086 0(2)	0.166 4(7)
C(7)	−0.114 1(3)	−0.111 9(2)	−0.130 8(7)
C(8)	−0.019 7(4)	−0.108 3(2)	−0.269 8(8)
C(9)	−0.216 2(4)	−0.114 0(2)	−0.250 2(7)
C(10)	−0.126 3(3)	−0.013 8(2)	−0.044 8(7)
C(11)	0.054 4(3)	0.148 7(2)	−0.035 4(7)
C(12)	0.133 4(3)	0.137 2(2)	0.122 4(8)
C(13)	0.197 9(4)	0.185 7(2)	0.157 1(11)
C(14)	0.148 7(4)	0.221 8(2)	0.006 2(12)
C(15)	0.184 1(4)	0.204 5(2)	−0.193 2(13)
C(16)	0.122 3(4)	0.153 3(2)	−0.224 5(9)
C(17)	0.030 2(3)	0.206 3(2)	0.013 7(9)
C(18)	−0.022 5(4)	0.212 8(2)	0.211 8(12)
C(19)	−0.038 9(4)	0.233 1(2)	−0.140 1(12)
C(20)	−0.039 1(3)	0.113 1(2)	−0.054 4(8)

Experimental

The general techniques used were the same as in other recent papers from this laboratory.[8]

trans-[PdCl$_2$(D-camo)$_2$].—A solution of D-camphor oxime (0.159 g, 0.95 mmol) and Na$_2$[PdCl$_4$]·4H$_2$O (0.146 g, 0.43 mmol) in methanol (7 cm^3) was set aside at room temperature for 22 h. The solid that separated was filtered off, washed with water (5 cm^3) and recrystallised from CH$_2$Cl$_2$–light petroleum (b.p. 60—80 °C) to give the required product as *yellow prisms* (0.172 g, 0.337 mmol, 78%), m.p. 185—188 °C (decomp.) (Found: C, 46.7; H, 6.65; Cl, 13.45; N, 5.5%; *M*, 531. C$_{20}$H$_{34}$Cl$_2$N$_2$O$_2$Pd requires C, 46.95; H, 6.7; Cl, 13.85; N, 5.45%; *M*, 512). I.r. spectrum (Nujol): ν(O–H) 3 240, ν(C=N) 1 678, ν(Pd–Cl) 342 cm^{-1}.

trans-[PdBr$_2$(D-camo)$_2$].—Treatment of the corresponding dichloride with a 20-fold excess of lithium bromide in acetone for 1 h followed by isolation and a further treatment with 20-fold excess of lithium bromide gave the required dibromide as *golden-yellow prisms* from dichloromethane–light petroleum (b.p. 60—80 °C). Yield 79% (Found: C, 40.25; H, 5.65; Br, 26.6; N, 4.5%, *M*, 601. C$_{20}$H$_{34}$Br$_2$N$_2$O$_2$Pd requires C, 40.0; H, 5.7; Br, 26.6; N, 4.65%; *M*, 601). I.r. spectrum (Nujol): (νO–H) 3 300, ν(C=N) 1 675,ν(Pd–Br) 255 cm^{-1}.

trans-[PdI$_2$(D-camo)$_2$].—This was made similarly in 41% yield as orange needles from dichloromethane–light petroleum (b.p. 60—80 °C) (Found: C, 34.9; H, 5.0; I, 36.2; N, 3.95%; *M*, 690. C$_{20}$H$_{34}$I$_2$N$_2$O$_2$Pd requires C, 34.6; H, 4.95; I, 36.55; N, 4.05%; *M*, 695).

Crystal Data.—C$_{20}$H$_{34}$Cl$_2$N$_2$O$_2$Pd, $M = 511.8$, Orthorhombic, $a = 1\,263.1(3)$, $b = 2\,610.5(10)$, $c = 685.3(2)$ pm, $U = 2.2596(12)$ nm^3, $Z = 4$, $D_c = 1.504$ Mg m^{-3}, $F(000) = 1\,056$, space group $P2_12_12_1$, Mo-K_α radiation, graphite monochromatised, $\lambda = 71.069$ pm, $\mu(\text{Mo-}K_\alpha) = 1\,065$ m^{-1}.

Data Collection.—Cell dimensions and their standard deviations were obtained by least-squares treatment of the diffractometer setting angles of 15 reflections with $35 < 2\theta < 40°$. The 2 317 independent reflections having $5 < 2\theta < 50°$ were measured in the ω—2θ scan mode, with scans running from 0.8° below $K_{\alpha1}$ to 0.8° above $K_{2\alpha}$.

Structure Analysis.—The data were corrected for Lorentz, polarisation, and absorption effects and the 2 081 reflections having $I > 3\sigma(I)$ were used in the structure analysis, using the SHELX program system.[9] Least-squares refinement of non-hydrogen atoms, with allowance for anisotropic vibrations, converged at $R = 0.037$, $R' = 0.053$. The 32 hydrogen atoms attached to carbon were introduced in idealised positions with C–H = 108 pm, $U_{\text{iso.}} = 500$ pm^2, and with tetrahedral geometry of the carbon atoms to which they were attached. The two remaining oxime hydrogens were then located on a difference map and introduced into the refinement, their co-ordinates and isotropic temperature factors permitted to refine. Final convergence was at $R = 0.025$, $R' = 0.025$. The enantiomorphic (L-camphor) structure converged at $R = 0.028$, $R' = 0.028$, and could have been rejected on the basis of Hamilton's significance test, had the absolute configuration been unknown. The atomic co-ordinates and estimated standard deviations of the non-hydrogen atoms and of the two independently refined hydrogen atoms are given in Table 2.

Acknowledgements

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