Crystal and Molecular Structure of *cis*-Dichlorobis[methylamino(methoxy)carbene]palladium(II)

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The title compound has been synthesized and its *X*-ray structure determined. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to *R* 4.7% for 1 947 independent reflections. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions: $a = 8.45(1)$, $b = 8.26(1)$, $c = 9.19(1)$ Å, $\alpha = 84.8(1)$, $\beta = 105.2(1)$, $\gamma = 106.7(1)°$, $Z = 2$. Co-ordination around palladium is square planar and involves two carbene carbons [Pd–C(1) 1.953(8), Pd–C(4) 1.972(10) Å] and two chlorine atoms [Pd–Cl(1) 2.359(4), Pd–Cl(2) 2.390(4) Å]. C–N Distances in the carbene ligands are 1.32(1) and 1.29(1) Å, and C–O distances 1.32(1) and 1.34(1) Å.

STUDIES on carbene complexes of transition metals have been critically evaluated in some recent reviews,[1,2] and structures interpreted in terms of chemical bonds. However, neither in these reviews nor in subsequent reports [3-7] have non-chelate *cis*-biscarbene complexes been considered from the structural point of view. We have therefore determined the crystal structure of such a compound and now report the structure of the title compound.

EXPERIMENTAL

Preparation of the Complex.—A methanolic solution of K_2PdCl_4 was allowed to react with a small excess of methyl isocyanide obtained by the method of ref. 8. A white product, identified (analysis, i.r.) as $[Cl_2(CH_3NC)_2Pd]$, was precipitated, but shortly redissolved.

The solution was allowed to evaporate very slowly and, after several weeks, pale yellow crystals were obtained. Analysis indicated the formula $C_6H_{14}Cl_2N_2O_2Pd$ (C, 21.45; H, 4.2; N, 9.5. $C_6H_{14}Cl_2N_2O_2Pd$ requires C, 22.28; H, 4.36; N, 8.86%). Prismatic pale yellow crystals suitable for *X*-ray diffraction analysis were obtained by recrystallization from ethanol.

Crystal Data.—$C_6H_{14}Cl_2N_2O_2Pd$, $M = 323.5$, $a = 8.45(1)$, $b = 8.26(1)$, $c = 9.19(1)$ Å, $\alpha = 84.8(1)$, $\beta = 105.2(1)$, $\gamma = 106.7(1)°$, $U = 592.8$ Å^3, $D_c = 1.81$, $Z = 2$, $D_m = 1.78$ g cm^{-3}, $F(000) = 320$. Cu-K_α radiation, $\bar{\lambda} = 1.5418$; $\mu(\text{Cu-}K_\alpha) = 169.8$ cm^{-1}. Space group $P\bar{1}$.

Crystallographic Measurements.—Rotation and Weissenberg photographs, obtained by rotation around [001], were used to determine approximate unit-cell dimensions. These values and intensity data were obtained by use of an on-line Siemens AED single-crystal diffractometer, with Ni-filtered Cu radiation and the ω—2θ scan technique. Of 2 146 independent reflections, 1 947, having $I > 2\sigma(I)$, were considered observed and used in the refinement. A standard reflection was monitored every 20 reflections to check the stability of the instrument, of the crystal, and of its alignment. The usual Lorentz and polarization corrections were applied to the structure amplitudes. Corrections for absorption were not considered necessary in view of the small crystal size (mean radius of cross-section 0.0625 mm; $\mu\bar{r}$ 1.06). The observed structure amplitudes were brought to an absolute scale by use of Wilson's statistical method.

Structure Analysis.—The structure was solved by the heavy-atom technique. The co-ordinates of Pd, Cl(1), and Cl(2) were determined from a three-dimensional Patterson map (*R* 22.4%). A subsequent electron-density synthesis phased on these atoms revealed the whole structure, excluding hydrogen atoms. Six cycles of least-squares block-diagonal refinement with isotropic thermal parameters improved the conventional *R* from 15.0 to 8.4%. This was further reduced to 5.2% after five cycles with anisotropic thermal parameters. At this stage a difference-Fourier map was computed and revealed the positions of all the hydrogen atoms. Isotropic refinement of these was attempted, but five cycles of least-squares, in which the *R* factor was constant at 4.8%, brought about an obvious deterioration in the bonding geometry of the four methyl groups. Least-squares refinement was therefore carried out with the two imine hydrogens, giving *R* 4.8%. Afterwards, introduction of the methyl hydrogen atoms, which were located in the ΔF map, gave a final *R* of 4.7%. The isotropic thermal parameters for these methyl hydrogen atoms were derived empirically from the ΔF map.

Atomic scattering factors used throughout were taken from ref. 9 for non-hydrogen atoms, and from ref. 10 for hydrogen atoms. Positional and thermal parameters are listed in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21380 (9 pp., 1 microfiche).[†]

All calculations were performed on a CDC 6 600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, with programs written by Immirzi.[11]

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RESULTS AND DISCUSSION

I.r. Spectra.—The i.r. spectrum, obtained on a Perkin-Elmer 457 instrument (KBr disc), is characterized by the following bands (cm^{-1}): ν(NH) 3 265s, 3 125w; ν(CH_3) 2 940mw; ν(CN) 1 565ms, sh; and ν(CO) 1 255s. The particularly high values of the ν(CN) and ν(CO) frequencies are in agreement with the multiple character of these bonds. Other bands appear at 1 590s, 1 468ms, 1 357ms, 1 165ms, 1 143m, and 1 005m cm^{-1}. Absorptions at 270m and 285mw cm^{-1} can be attributed to ν(Pd–Cl). The low values of these frequencies, which agree with those reported [7] for similar complexes, are due to the high *trans*-influence of the carbene ligands, which has been shown to be similar to that of the phosphine ligands.[5]

X-*Ray Structure.*—A clinographic projection of the structure is shown in the Figure. Interatomic distances and angles are given in Table 2. The complex molecule consists of three planar parts: the co-ordination environment of the metal atom, which is square planar, and the two planar carbene ligands. Table 3 lists the equations of the main best least-squares planes with displacements of relevant atoms from them.

TABLE 1

Fractional atomic co-ordinates (× 10^4 for non-hydrogen atoms and × 10^3 for hydrogen atoms) and temperature factors,* with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	411(1)	4 030(1)	2 295(1)	2.77(2)	3.54(2)	2.62(2)	1.29(2)	0.79(2)	−0.02(2)
Cl(1)	−2 171(3)	1 930(3)	2 252(2)	3 46(9)	4.61(10)	3.78(9)	0.67(8)	1.07(7)	0.13(8)
Cl(2)	−907(3)	6 288(3)	1 912(2)	3.69(9)	4.03(9)	3.68(9)	2.02(7)	0.89(7)	−0.22(7)
C(1)	2 615(10)	5 654(10)	2 325(9)	3.65(35)	3.26(35)	3.01(33)	1.31(28)	0.18(27)	−0.11(26)
N(1)	3 279(9)	5 924(9)	1 146(7)	3.21(29)	4.84(36)	3.33(30)	1.28(26)	1.02(24)	−0.13(25)
C(2)	4 901(12)	7 088(14)	1 040(11)	3.16(38)	6.48(57)	5.10(49)	0.99(37)	1.18(34)	0.29(40)
O(1)	3 673(8)	6 602(9)	3 444(7)	3.96(28)	6.11(36)	4.18(29)	0.86(27)	1.08(23)	−1.55(25)
C(3)	3 075(15)	6 646(16)	4 795(11)	6.41(60)	8.49(74)	3.48(43)	0.85(53)	1.34(41)	−2.24(45)
C(4)	1 481(11)	2 166(11)	2 485(10)	3.82(37)	3.54(37)	4.03(38)	1.29(30)	1.03(30)	0.01(29)
N(2)	1 768(10)	1 638(9)	1 329(8)	5.29(39)	4.15(35)	3.83(33)	2.24(30)	1.82(28)	0.34(26)
C(5)	2 504(14)	185(13)	1 385(12)	6.53(57)	4.26(46)	6.34(56)	2.86(42)	2.45(46)	−0.44(39)
O(2)	2 000(9)	1 367(9)	3 785(7)	5.46(33)	4.58(34)	3.44(27)	2.62(27)	0.77(24)	0.57(23)
C(6)	1 761(15)	1 880(15)	5 160(10)	6.56(59)	6.80(62)	3.16(41)	2.21(48)	0.67(38)	0.59(38)

(*b*) Hydrogen atoms

	x/a	y/b	z/c	B/Å^2		x/a	y/b	z/c	B/Å^2
H(1)	284(14)	482(14)	53(12)	5.78 (2.85)	H(8)	367	35	226	8.25
H(2)	158(13)	224(13)	34(11)	6.45 (2.58)	H(9)	197	565	459	9.08
H(3)	514	826	135	7.27	H(10)	350	790	494	9.08
H(4)	560	691	177	7.27	H(11)	358	586	507	9.08
H(5)	496	719	7	7.27	H(12)	169	78	583	8.18
H(6)	252	8	53	8.25	H(13)	56	183	509	8.18
H(7)	177	−92	190	8.25	H(14)	255	290	541	8.18

* Anisotropic thermal parameters are in the form: exp $-0.25(h^2\beta_{11}a^{*2} + \cdots + 2kl\beta_{23}b^*c^*)$.

The values of two Pd–Cl distances are very close to that reported in ref. 3 [2.387(1) Å], but are among the highest observed for other Pd complexes [12-15] and significantly greater than the sum of Pauling's covalent radii (2.31 Å).[16] This can be explained by the considerable *trans*-effect exercised by the carbene carbon atoms, which produces a loosening of the Pd–Cl bonds. The Pd–C(1) [1.95(1)] and Pd–C(4) [1.97(1) Å] distances are in the middle of the range (1.92—2.04 Å) reported [12,17-19] for Pd–C(σ) bonds. All these bonds tend to be less than the sum of the relevant covalent radii [Pd^{II}–C(sp^2) 2.05 Å], indicating some additional π character. This fact has been already observed [20] for the complex [{(PhNH)(EtO)C}(Et_3P)$PtCl_2$], in which Pt–C is 1.98 Å.

There are small but significant differences between the pairs of Pd–Cl and Pd–C distances, the shortest being mutually *trans*. Pd–Cl(2) is a little longer than Pd–Cl(1), probably as a consequence of Cl(2) being involved in hydrogen bonding, whereas Cl(1) shows no such interaction.

As expected the non-hydrogen atoms are planar in both carbene ligands and their planes are roughly perpendicular to the co-ordination plane, the torsion angles around C(1)–Pd and C(4)–Pd being 80.4 and 82.4°. It is possible that the orientation of the carbene ligands is conditioned by the hydrogen bonds they form with the Cl(2) chlorine of an adjacent molecule and by the interaction (if it is present) of the imine protons with the metal.

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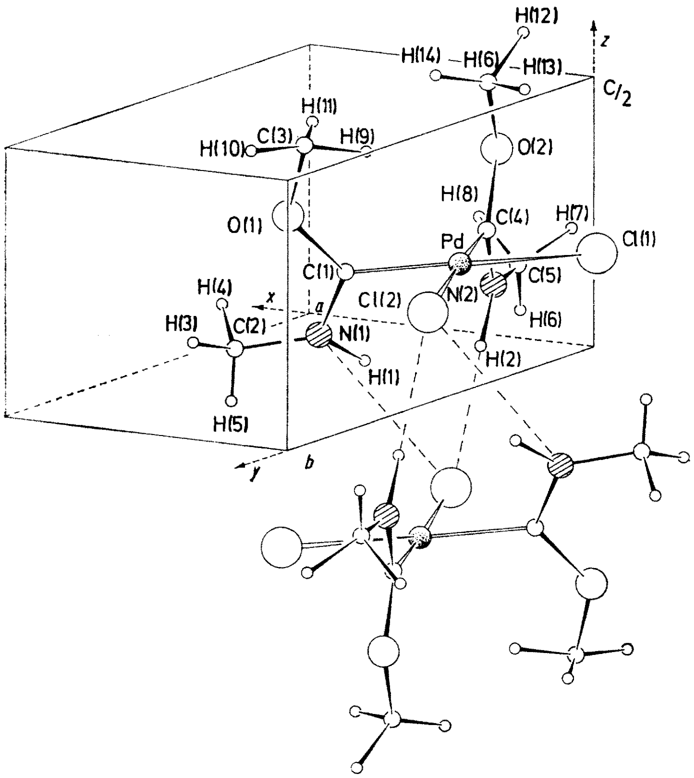
As in other alkoxy- and amino-carbene complexes,[20-23] the values of the C–O and C–N distances indicate some π delocalization along the O–C–N system, with somewhat greater double-bond character for C–N. This is in agreement with the fact that the more electropositive lone-pair of an α-nitrogen atom interacts more strongly with the C(sp^2) p_z orbital, than does the less electropositive lone-pair of the α-oxygen atom of an alkoxy-group.[1] From these π interactions, together with those involving the palladium *d* orbitals, the carbene complex acquires sufficient thermal stability.[1]



The angles at the carbene carbons C(1) and C(4) (109 and 114°) are as expected.[21-23] The N(1)–C(2), N(2)–C(5), O(1)–C(3), and O(2)–C(6) distances (Table 2) correspond to normal single bonds.

The two imine hydrogens H(1) and H(2) are 2.84 and 2.94 Å from palladium, and these distances are less than the sum of the van der Waals radii (3.10 Å), indicating some metal–hydrogen interaction. However, no conclusion can be reached about the Pd–H(Me) distances since the co-ordinates of these hydrogen atoms could not be refined by least squares. These atom positions correspond to well defined peaks in the final difference-Fourier map. The shortest contact formed by the hydrogens of the C(6) methyl group with palladium is 3.0 Å, while the shortest distance between

TABLE 2

Interatomic distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Bond distances

Pd–Cl(1)	2.359(4)	N(2)–H(2)	0.99(10)
Pd–Cl(2)	2.390(4)	C(2)–H(3)	0.98
Pd–C(1)	1.953(8)	C(2)–H(4)	0.80
Pd–C(4)	1.972(10)	C(2)–H(5)	0.90
C(1)–O(1)	1.316(9)	C(3)–H(9)	1.04
C(1)–N(1)	1.320(12)	C(3)–H(10)	1.01
N(1)–C(2)	1.452(11)	C(3)–H(11)	0.86
O(1)–C(3)	1.465(14)	C(5)–H(6)	0.80
C(4)–O(2)	1.343(11)	C(5)–H(7)	1.09
C(4)–N(2)	1.287(13)	C(5)–H(8)	1.08
N(2)–C(5)	1.494(15)	C(6)–H(12)	1.05
O(2)–C(6)	1.448(14)	C(6)–H(13)	0.99
N(1)–H(1)	1.04(11)	C(6)–H(14)	0.92

(*b*) Bond angles

Cl(1)–Pd–Cl(2)	93.5(1)	H(3)–C(2)–H(4)	91
Cl(1)–Pd–C(4)	86.7(3)	H(3)–C(2)–H(5)	104
Cl(2)–Pd–C(1)	90.1(3)	H(4)–C(2)–H(5)	128
C(1)–Pd–C(4)	89.6(4)	O(1)–C(3)–H(9)	101
Pd–C(1)–N(1)	122.2(6)	O(1)–C(3)–H(10)	97
Pd–C(1)–O(1)	128.5(6)	O(1)–C(3)–H(11)	81
O(1)–C(1)–N(1)	109.3(7)	H(9)–C(3)–H(10)	143
C(1)–N(1)–C(2)	127.0(7)	H(9)–C(3)–H(11)	84
C(1)–N(1)–H(1)	108(6)	H(10)–C(3)–H(11)	131
C(2)–N(1)–H(1)	118(6)	N(2)–C(5)–H(6)	105
C(1)–O(1)–C(3)	117.7(8)	N(2)–C(5)–H(7)	110
Pd–C(4)–N(2)	121.0(7)	N(2)–C(5)–H(8)	111
Pd–C(4)–O(2)	124.7(6)	H(6)–C(5)–H(7)	116
O(2)–C(4)–N(2)	114.3(8)	H(6)–C(5)–H(8)	119
C(4)–N(2)–C(5)	123.6(8)	H(7)–C(5)–H(8)	96
C(4)–N(2)–H(2)	121(6)	O(2)–C(6)–H(12)	103
C(5)–N(2)–H(2)	115(6)	O(2)–C(6)–H(13)	113
C(4)–O(2)–C(6)	118.8(8)	O(2)–C(6)–H(14)	107
N(1)–C(2)–H(3)	118	H(12)–C(6)–H(13)	92
N(1)–C(2)–H(4)	106	H(12)–C(6)–H(14)	125
N(1)–C(2)–H(5)	109	H(13)–C(6)–H(14)	116

(*c*) Pd–H interactions

Pd · · · H(1)	2.84(12)	Pd · · · H(11)	3.28
Pd · · · H(2)	2.94(12)	Pd · · · H(13)	3.00
Pd · · · H(9)	2.45	Pd · · · H(14)	3.18

(*d*) Hydrogen bonds

N(1)–H(1) · · · Cl(2^{I})	3.336(10)	N(1)–H(1) · · · Cl(2^{I})	139.6
N(2)–H(2) · · · Cl(2^{i})	3.315(10)	N(2)–H(2) · · · Cl(2^{I})	174.3

Superscript I denotes atom at $\bar{x}$, $1 - y$, $\bar{z}$.

TABLE 3

Equations of the best least-squares planes of the three planar parts of the complex, and in square brackets deviations (Å) of relevant atoms from the planes. Equations are in the form $AX + BY + CZ = D$, where X, Y, Z are the co-ordinates in Å referred to orthogonal axes, and obtained from the triclinic ones by applying the matrix: $\sin\gamma, 0, -\sin\alpha\cos\beta^*|\cos\gamma, 1, \cos\alpha|0, 0, \sin\alpha\sin\beta^*$

Plane (*a*): Pd, Cl(1), Cl(2), C(1), C(4)

$$0.0733X - 0.1134Y - 0.9908Z = -2.3901$$

[Pd −0.028, Cl(1) −0.017, Cl(2) −0.008, C(1) −0.016, C(4) 0.068]

Plane (*b*): C(1)—(3), N(1), O(1)

$$-0.3802X + 0.8585Y - 0.3442Z = 2.3386$$

[C(1) −0.022, N(1) 0.000, O(1) −0.061, C(2) 0.004, C(3) 0.079; H(1) −0.465]

Plane (*c*): C(4)—(6), N(2), O(2)

$$-0.8985X - 0.4074Y - 0.1635Z = -1.6128$$

[C(4) 0.015, N(2) −0.017, O(2) −0.010, C(5) 0.012, C(6) 0.001, H(2) −0.121]

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palladium and the hydrogens of the C(3) methyl group is 2.45 Å. This last contact is very short indeed, and although it is possible that it is incorrect, contacts of this kind have been found previously, *e.g.* 2.30 Å in bromo(1,2,3,4-tetrakismethoxycarbonylbuta-1,3-dienyl)bis(triphenylphosphine)palladium.[18]

The molecules are linked in centrosymmetric pairs by hydrogen bonds of the type NH···Cl involving the imine nitrogen atoms N(1) and N(2), and chlorine Cl(2) (Figure). The packing of these pairs is determined by normal van der Waals interactions.

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