

and reflects the considerable disorder associated with the *tert*-butoxy groups. Molecular motion of *tert*-butoxy groups has previously been observed (Weiss, Alsdorf, Kühr & Grützmaier, 1968) in a ¹H wide-line NMR study of the compound [(CH₃)COK]₄. In this case, the NMR results above 243 K indicate that rotation of the *tert*-butoxy group as a whole is coupled with rotation of individual methyl groups.

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Chloro[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*C,N*]- [4-(dimethylamino)pyridine]palladium(II)

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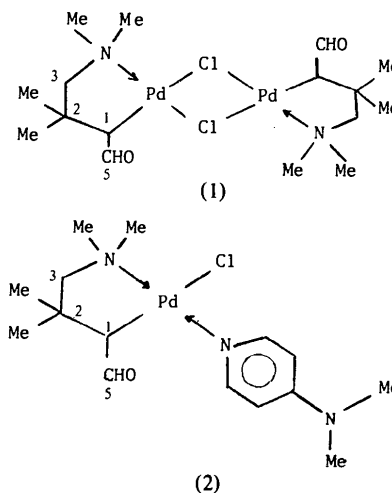
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Abstract. Pd(C₇H₁₀N₂)(C₈H₁₆NO)Cl, C₁₅H₂₆ClN₃OPd, *M_r* = 406.2, monoclinic, *P*2₁/*n*, *a* = 10.762 (1), *b* = 23.994 (5), *c* = 6.989 (1) Å, β = 98.46 (2)°, *U* = 1785.2 Å³, *D_c* = 1.51 g cm⁻³, *Z* = 4, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 29.0 cm⁻¹, *F*(000) = 832, space group determined uniquely from systematic absences: *h*0*l*, *h* + *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1. *R* = 0.028 for 2449 reflections [with *I* > 3σ(*I*)] measured by diffractometer. The palladium atom has a slightly distorted square-planar configuration in a five-membered chelate ring that has an envelope conformation. Principal bond lengths are Pd–Cl(*trans* to C) 2.413 (1), Pd–C(1) 2.052 (4), Pd–N(1) 2.086 (3), and Pd–N(2) 2.038 (3) Å. The X-ray data establish that there is a significant interaction between the palladium and aldehyde carbon C(5), Pd...C(5) 2.664 (4) Å, C(5)–C(1)–Pd 97.3 (2)°. The Pd–C(1)–C(5)–O torsion angle is 96.0 (5)°.

Introduction. We have previously reported (Alyea, Dias, Ferguson, McAlees, McCrindle & Roberts, 1977) the synthesis and X-ray structure analysis of di-*μ*-chloro-bis[1-formyl-2,2-dimethyl-3-(dimethylamino)propyl-*C,N*]dipalladium(II) (1), in which there appears to be a direct interaction between the palladium atom and the carbon atom of the formyl group. Interactions of this type have been discussed (Green, 1968; Pannell, Cassias, Crawford & Flores, 1976) in

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terms of a direct overlap of metal *d* orbitals with π orbitals of the carbonyl function. Alternatively, a σ–π conjugative interaction of the Pd–C bond with the carbonyl group could be invoked to explain the properties of such systems. The latter description has been widely applied in the rationalization of the spectral properties and reactivities of organometallic derivatives of non-transition metals (Meyer, Gorrichon-Guigon & Maroni, 1980). In the course of an investigation (McCrindle & McAlees, 1982) of the influence of changes in the palladium coordination sphere on this interaction, a series of compounds related to (1), and including the title compound (2), has now been



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Table 1. *Final fractional coordinates* ($\times 10^5$ for Pd, Cl; $\times 10^4$ for the other atoms) for C₁₅H₂₆ClN₃OPd with standard deviations in parentheses

	x	y	z	B_{eq} (\AA^2)*
Pd	28478 (2)	12778 (1)	3467 (4)	3.20 (2)
Cl	6572 (9)	15248 (5)	1214 (16)	4.7 (1)
C(1)	4731 (3)	1096 (2)	707 (5)	3.8 (2)
C(2)	5427 (3)	1653 (2)	884 (4)	3.9 (2)
C(3)	4856 (4)	1999 (2)	2379 (6)	4.3 (2)
C(4)	6841 (4)	1579 (2)	1615 (7)	5.4 (2)
C(5)	4755 (4)	731 (2)	2381 (7)	4.8 (2)
C(6)	5256 (4)	1937 (2)	-1111 (6)	5.5 (2)
C(7)	2918 (4)	2496 (2)	1104 (7)	5.1 (2)
C(8)	2969 (4)	1923 (2)	3938 (6)	5.1 (2)
C(9)	2954 (3)	514 (1)	-2999 (5)	3.8 (2)
C(10)	2636 (3)	88 (2)	-4270 (5)	3.7 (2)
C(11)	1684 (3)	-293 (1)	-3966 (5)	3.4 (2)
C(12)	1148 (3)	-205 (2)	-2263 (6)	3.9 (2)
C(13)	1513 (3)	234 (2)	-1095 (6)	4.0 (2)
C(14)	312 (4)	-1092 (2)	-4890 (6)	4.4 (2)
C(15)	1927 (4)	-814 (2)	-6888 (6)	4.9 (2)
N(1)	3434 (3)	1971 (1)	2046 (4)	3.7 (2)
N(2)	2407 (3)	606 (1)	-1405 (5)	3.7 (2)
N(3)	1318 (3)	-714 (1)	-5194 (4)	3.9 (2)
O	5027 (3)	853 (1)	4094 (5)	5.7 (2)

$$* B_{\text{eq}} = 8\pi^2 (U_{11} + U_{22} + U_{33})/3.$$

Table 2. *Interatomic distances* (\AA) *and angles* ($^\circ$)

The hydrogen atoms were refined with the carbon atoms to which they are attached.

Pd-Cl	2.413 (1)	N(1)-C(7)	1.492 (5)
Pd-C(1)	2.052 (4)	N(1)-C(8)	1.486 (5)
Pd-N(1)	2.086 (3)	N(2)-C(9)	1.352 (5)
Pd-N(2)	2.038 (3)	N(2)-C(13)	1.354 (5)
C(1)-C(2)	1.528 (5)	C(9)-C(10)	1.364 (5)
C(1)-C(5)	1.459 (6)	C(10)-C(11)	1.413 (5)
C(2)-C(3)	1.532 (6)	C(11)-C(12)	1.413 (5)
C(2)-C(4)	1.543 (6)	C(11)-N(3)	1.346 (5)
C(2)-C(6)	1.539 (6)	C(12)-C(13)	1.355 (5)
C(3)-N(1)	1.515 (5)	N(3)-C(14)	1.451 (5)
C(5)-O	1.225 (5)	N(3)-C(15)	1.455 (5)
Cl-Pd-C(1)	176.2 (1)	C(3)-N(1)-C(7)	109.4 (3)
Cl-Pd-N(1)	93.0 (1)	C(3)-N(1)-C(8)	109.4 (3)
Cl-Pd-N(2)	90.9 (1)	C(7)-N(1)-C(8)	107.8 (3)
C(1)-Pd-N(1)	83.6 (1)	Pd-N(1)-C(7)	111.2 (2)
C(1)-Pd-N(2)	92.5 (1)	Pd-N(1)-C(8)	109.4 (3)
N(1)-Pd-N(2)	175.4 (1)	Pd-N(2)-C(9)	122.2 (2)
Pd-C(1)-C(2)	106.7 (3)	Pd-N(2)-C(13)	122.3 (2)
Pd-C(1)-C(5)	97.3 (2)	C(9)-N(2)-C(13)	115.5 (3)
C(2)-C(1)-C(5)	120.6 (3)	N(2)-C(9)-C(10)	124.1 (3)
C(1)-C(2)-C(3)	106.8 (3)	C(9)-C(10)-C(11)	120.3 (3)
C(1)-C(2)-C(4)	112.0 (3)	C(10)-C(11)-N(3)	122.7 (3)
C(3)-C(2)-C(4)	108.2 (3)	C(10)-C(11)-C(12)	115.1 (3)
C(1)-C(2)-C(6)	108.8 (3)	N(3)-C(11)-C(12)	122.2 (3)
C(3)-C(2)-C(6)	111.8 (4)	C(11)-N(3)-C(14)	122.0 (3)
C(4)-C(2)-C(6)	109.4 (4)	C(11)-N(3)-C(15)	121.2 (3)
C(2)-C(3)-N(1)	111.6 (3)	C(14)-N(3)-C(15)	116.8 (3)
C(1)-C(5)-O	127.8 (4)	C(11)-C(12)-C(13)	120.4 (3)
C(3)-N(1)-Pd	109.7 (2)	C(12)-C(13)-N(2)	124.5 (4)

prepared. Examination of the IR spectra of these compounds has shown that $\nu(\text{C}=\text{O})$ can vary over the range *ca* 1620 to *ca* 1650 cm^{-1} (Nujol mulls). Since (2) shows one of the lowest values for $\nu(\text{C}=\text{O})$ (1621 and 1631 cm^{-1}) we decided to elucidate its structure for comparison with that of (1) [$\nu(\text{C}=\text{O})$ 1640 cm^{-1}], in order to determine if a frequency difference of this magnitude reflects any significant difference in the palladium-formyl-group interaction in these compounds. The present structure determination reveals that the difference is minimal.

Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections (with θ in the range 10–20°) measured on a Hilger & Watts four-circle Y290 diffractometer. Intensity data were collected in our usual way (Alyea *et al.*, 1977) with a small crystal to a maximum θ of 20° and 2572 unique data were obtained. After corrections for Lorentz, polarization effects and absorption, the data with $I > 3\sigma(I)$, 2449, were labelled observed and used in structure solution and refinement. All calculations were carried out on the Amdahl V5 computer with our programs for data reduction; the *SHELX* (Sheldrick, 1976) program system was used in subsequent calculations.

The coordinates of the Pd and Cl atoms were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement was by full-matrix least-squares calculations initially with isotropic and then with anisotropic vibration parameters. A difference map computed at an intermediate stage in the refinement revealed maxima in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealized positions (C–H 0.95 \AA) and included in the final rounds of calculations. Only an overall isotropic thermal parameter was refined. In the final three refinement cycles a weighting scheme of the form $w = 1/(\sigma^2 F + pF^2)$ was employed where the final p parameter was 0.0004. Scattering factors used in the structure-factor calculations were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) and allowance was made for anomalous dispersion (Cromer & Liberman, 1970). Refinement converged with $R = 0.0276$ and $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0.0299$ for the 2449 reflections with $I > 3\sigma(I)$. A final difference map was devoid of any significant features. Positional parameters are given in Table 1 and details of molecular dimensions are in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and the calculated hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36813 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The crystal structure (Fig. 1) of (2) contains discrete molecules (Fig. 2) in which the dimethylaminopyridine ligand bonds to the metal *via* the pyridine nitrogen atom as suggested by our ¹H NMR data in solution (McCrindle & McAlees, 1982). The palladium atom has a slightly distorted square-planar coordination in which the *cis* angles at Pd are in the range 83.6–93.0(1)°. The palladium is not significantly removed [0.006(2) Å] from the plane of the atoms bonded to it.

The geometry of the five-membered ring formed by the dimethylaminopropyl ligand and Pd, and the orientation of the axial CHO moiety are very similar to those reported for the corresponding chloro-bridged dimer (1) (Alyea *et al.*, 1977). Thus the five-membered ring adopts an envelope conformation with C(2) 0.65(1) Å below the plane of C(1), C(3), N(1) and Pd. The geometry at N(1) is close to tetrahedral and the Pd–(chelate-ring *N*-methyl) contacts are very similar: Pd···C(7) 2.970(4), Pd···C(8) 2.936(4) Å. The

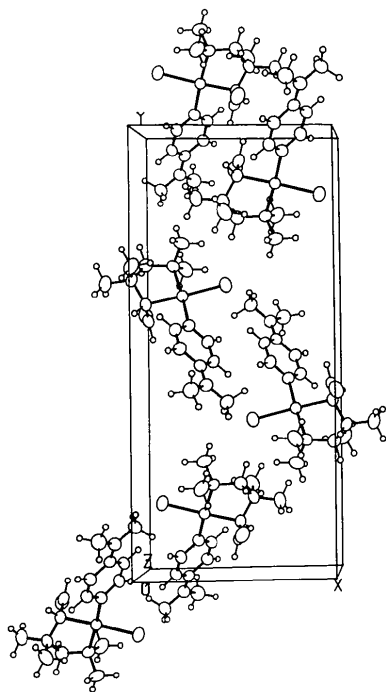


Fig. 1. View of the crystal structure of (2).

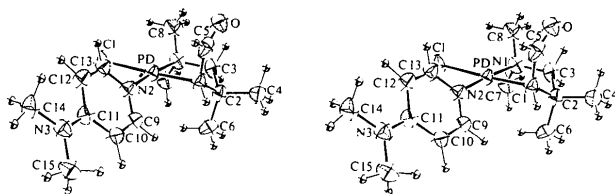


Fig. 2. Stereoview of a molecule of (2) showing the crystallographic numbering scheme.

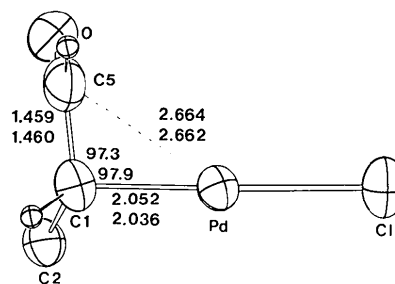


Fig. 3. Comparison of the dimensions around the formyl moiety in (1) and in (2) (lower and upper numbers respectively) (Å and deg).

geometry at C(1) is irregular and there are severe distortions from tetrahedral valence angles [Pd–C(1)–C(5) 97.3(2), Pd–C(1)–C(2) 106.7(3) and C(2)–C(1)–C(5) 120.6(3)°]. The dimensions and orientation of the aldehyde group are compared with those found in (1) in Fig. 3. In both molecules the C(1)–C(5) distance is significantly shorter than anticipated for a normal C_{sp³}–C_{sp²} single bond (1.505 Å) (Bartell & Bonhan, 1960), the Pd···C(5) contacts are essentially identical, and the Pd–C(1)–C(5) angles are much less than tetrahedral. The only small differences between the two systems are that the Pd–C(1)–C(5)–O torsion angle is 96.0(5)° in (2) and 100.8° in (1), and that the Pd–C(1) distance is lengthened on going from (1) to (2) in accord with the fact that in (2) the Cl atom is terminal whereas in (1) it is bridging.

The dimensions of the dimethylaminopyridine moiety are consistent with its having substantial quinoid character; thus bonds C(9)–C(10) 1.364(5), C(12)–C(13) 1.355(5), C(11)–N(3) 1.346(5) Å more closely resemble double bonds than single ones and N(3) has planar geometry. The pyridine ligand plane makes an angle of 52(1)° with the Pd coordination plane; this conformation appears to minimize interaction between the pyridine ring and the aldehyde moiety. The remaining dimensions in the molecule are in accord with previously determined values and are unexceptional.

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Structure of Carbonyldichloro(*p*-chlorophenyl isocyanide)bis(triphenylphosphine)ruthenium(II) Ethanol Solvate

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Abstract. C₄₄H₃₄Cl₃NOP₂Ru·C₂H₆O, *M_r* = 908·15, monoclinic, *P*2₁/*c*, *a* = 12·257 (1), *b* = 18·547 (2), *c* = 18·744 (4) Å, β = 93·33 (1)°, *V* = 4254 (2) Å³, *T* = 295 ± 1 K, *Z* = 4, *D_c* = 1·41 Mg m⁻³, μ(Mo *K*α) = 0·661 mm⁻¹, *R* = 0·066 for 2183 observed reflections. The complex is monomeric, with octahedral coordination geometry. Ru–P distances are 2·420 (6) and 2·422 (6) Å; Ru–Cl *trans* to –CNR [2·460 (6) Å] is significantly longer than that *trans* to –CO [2·428 (6) Å]; Ru–CNR is 1·94 (2) Å. The isocyanide is non-linear [C–N–Ph 165 (2)°].

Introduction. An X-ray structure determination has been carried out on crystals grown from the product of a reaction in which it was hoped to prepare a chloro amino carbene complex of formula RuCl(CO){C(Cl)NMe₂}(CN-*p*-ClC₆H₄)(PPh₃)₂ (Wright & Roper, 1981). However, the analysis shows that the particular crystal selected for investigation is the dichloro isocyanide compound RuCl₂(CO)(CN-*p*-ClC₆H₄)(PPh₃)₂·ethanol.

Intensities from a crystal fragment, approximately 0·32 × 0·20 × 0·14 mm, were recorded with a Nonius CAD-4 diffractometer using Zr-filtered Mo *K*α radiation. Data were collected to the practical upper limit for the crystal (sin θ/λ 0·55 Å⁻¹) with a 2θ/ω scan, yielding 2183 unique observed reflections [*I* > 3σ(*I*), σ(*I*) = 20·116/NPI √*C* + *R*²*B*, where the number 20·116 is the maximum possible scan rate, NPI is the ratio of the maximum scan rate to the scan rate for the actual measurement, *C* = total count, *R* = ratio of scan time to background counting time (=2), *B* = total background counts] which were used in the full-matrix least-squares refinement.

The structure was solved using *MULTAN* (Main, Germain & Woolfson, 1970) to locate the five heaviest

atoms, followed by a 'difference' electron-density map to locate the remaining non-H atoms. An ethanol solvent molecule was also found to be present in the unit cell. In the initial least-squares refinement cycles the C and O atoms of the carbonyl ligand tended to merge towards each other to give an unrealistically short C–O distance, and the ethanol solvent molecule behaved similarly. These atoms were therefore repositioned by an analysis of the peak profiles of their partially overlapping peaks in a difference map. The resulting geometries were chemically reasonable, and these atoms have not been refined further. The possibility of lowering the σ cut-off limit was considered, but as there were only 60 reflections for which 2σ(*I*) < *I* < 3σ(*I*) it was felt that inclusion of these few extra reflections would do little to improve the resolution.

The final refinement cycles included anisotropic thermal parameters for all remaining non-H atoms except the C atoms of the phenyl rings which were constrained to be isotropic. H atoms were included in calculated positions (C–H 1·02 Å) but were not refined. Their isotropic *B* values were set 20% higher than that of the C atom to which each was bonded. Final residuals were *R* [= ∑ ||*F_o*| – |*F_c*|| / ∑ *F_o*] 0·066 and *R_w* [= (∑ *w* ||*F_o*| – |*F_c*||² / ∑ *w* |*F_o*|²)^{1/2}] 0·074 [*w* = 4|*F_o*|² / σ²(*F_o*)²]. No corrections were made for extinction or absorption effects [μ(Mo *K*α) = 0·661 mm⁻¹].

Atomic positional parameters are listed in Table 1.* Interatomic distances and angles are given in Table 2.

* Lists of structure factors, anisotropic thermal parameters, assigned H-atom positions and bond lengths and angles for phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36810 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.