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STRUCTURE OF *trans*-CHLORO-1,4-BIS(*p*-METHOXYPHENYL)-1,4-DIAZA-3-METHYLBUTADIENE-2-YL-BIS(TRIPHENYLPHOSPHINE)-PALLADIUM(II)

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Summary

The structure of the compound *trans*-[PdCl{$\overline{\mathrm{C}(=\mathrm{N}\text{-}p\text{-}\mathrm{C_6H_4OMe})\mathrm{C}}$(Me)=N-*p*-$\mathrm{C_6H_4OMe}$}$(\mathrm{PPh_3})_2$] was solved, using a conventional combination of Patterson and Fourier functions, least-squares refinements and electron density difference maps, to a reliability index R of 0.069 for the 2923 observed reflections collected by four-circle diffractometer. The palladium arom is surrounded in a roughly planar fashion by two *trans* phosphorus atoms, a chlorine atom, and a σ-bonded carbon atom of the diazabutadienyl group. This group assumes a *trans* configuration, the N=C—C=N fragment being virtually planar and nearly normal to the mean coordination plane. The Pd—ligand bond lengths are: Pd—C 1.98(1), Pd—Cl 2.41(1), Pd—P(1) 2.33(1) and Pd—P(2) 2.35(1) Å.

Introduction

The organic 1,4-diazabutadienes, such as those derived from condensation of primary amines with ethanedial or 2,3-butandione, have been reported on the basis of spectroscopic and dipole moment measurements [1,2] to assume preferentially a *trans*-configuration with *anti* N-substituents. We have prepared the complex *trans*-[PdCl{$\overline{\mathrm{C}(=\mathrm{N}\text{-}p\text{-}\mathrm{C_6H_4OMe})\mathrm{C}}$(Me)=N-*p*-$\mathrm{C_6H_4OMe}$}$(\mathrm{PPh_3})_2$] containing a σ-bonded 1,4-diaza-3-methylbutadiene-2-yl group [3], which was found to act as a chelating bidentate ligand towards a variety of transition metal ions to give a new type of binuclear compounds [4,5,6]. The diazabutadienyl moiety can be easily monoprotonated by strong mineral acids [3] and undergoes acid catalyzed hydrolysis only at the imino carbon atom not directly bonded to the central metal [7], at variance with the organic diazabutadienes which under the same experimental conditions are completely hydrolized. In no case was electrophilic cleavage of the Pd—C σ-bond observed.

We have now carried out an X-ray analysis of this complex in order (i) to ascertain the configuration of the diazabutadienyl group, and thus possible bonding interactions between the imino nitrogen atoms and Pd [8], and (ii) to see whether structural parameters could account for the special stability of the Pd—C σ-bond and the partial hydrolysis of the diazabutadienyl group, which may possibly be connected with π-interaction between the metal *d* electrons and the conjugated double-bond system.

Collection of X-ray data, solution of structure

The complex *trans*-$[\mathrm{PdCl}\{\overline{\mathrm{C}(=\mathrm{N}\text{-}p\text{-}\mathrm{C_6H_4OMe})\mathrm{C}}(\mathrm{Me})=\mathrm{N}\text{-}p\text{-}\mathrm{C_6H_4OMe}\}(\mathrm{PPh_3})_2]$ was prepared by a published method [3] and recrystallized from CH_2Cl_2/ethyl ether.

TABLE 1

CRYSTALLOGRAPHICALLY IMPORTANT DATA COLLECTION AND DATA PROCESSING INFORMATION

Molecular formula	$C_{53}H_{47}ClN_2O_2F_2Pd$
Molecular weight	947.72 g mol^{-1}
Crystal system	triclinic
Space group	$P\bar{1}$
Cell constants [a] (Mo—K_α, λ = 0.7107 Å) at 23°C	a = 14.889(12) Å b = 14.229(13) c = 11.023(7) α = 86.28(8)° β = 80.13(7) γ = 81.96(7)
Unit cell volume	2276.1 Å^3
Density	D_c = 1.38; D = 1.36 g cm^{-3}
$F(000)$	976
Standards for intensity control (every 90 min)	[2, 3, 0; 5, 3, 3; $\bar{5}$, $\bar{2}$, $\bar{4}$]
Max deviation of standards	4%
Scanning range for 2 θ	$6.0 \leqslant 2\theta \leqslant 44.0°$
Scan width for each reflection	$\Delta\, 2\theta = 1.40°$
Scan speed	0.04° sec^{-1}
Background time	20 sec.
Absorption coefficient	$\mu = 5.1$ cm^{-1}
Total number of data points collected	5566
Number above three standard deviations	2923
Number of total variables	265
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = 1$
Finale $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.069

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of 25 reflections.

Details of crystal data, measurement of intensity and data processing are summarized in Table 1.

The bright-yellow crystal (a parallelepiped of 0.12 × 0.26 × 0.12 mm^3) was mounted on a Philips PW 1100 fully automatic four-circle diffractometer with the $-b$ axis nearly coincident with ϕ-axis. The observed intensities and their variances were corrected for Lorentz and polarization effects and processed in the normal fashion [9]. No absorption correction was made since the μ value is low and no significant intensity variation for a given reflection was observed when rotating around the azimuthal angle ψ. The structure was solved using a conventional combination of Patterson and Fourier functions, least-squares refinements and electron density difference functions. The largest shift in any

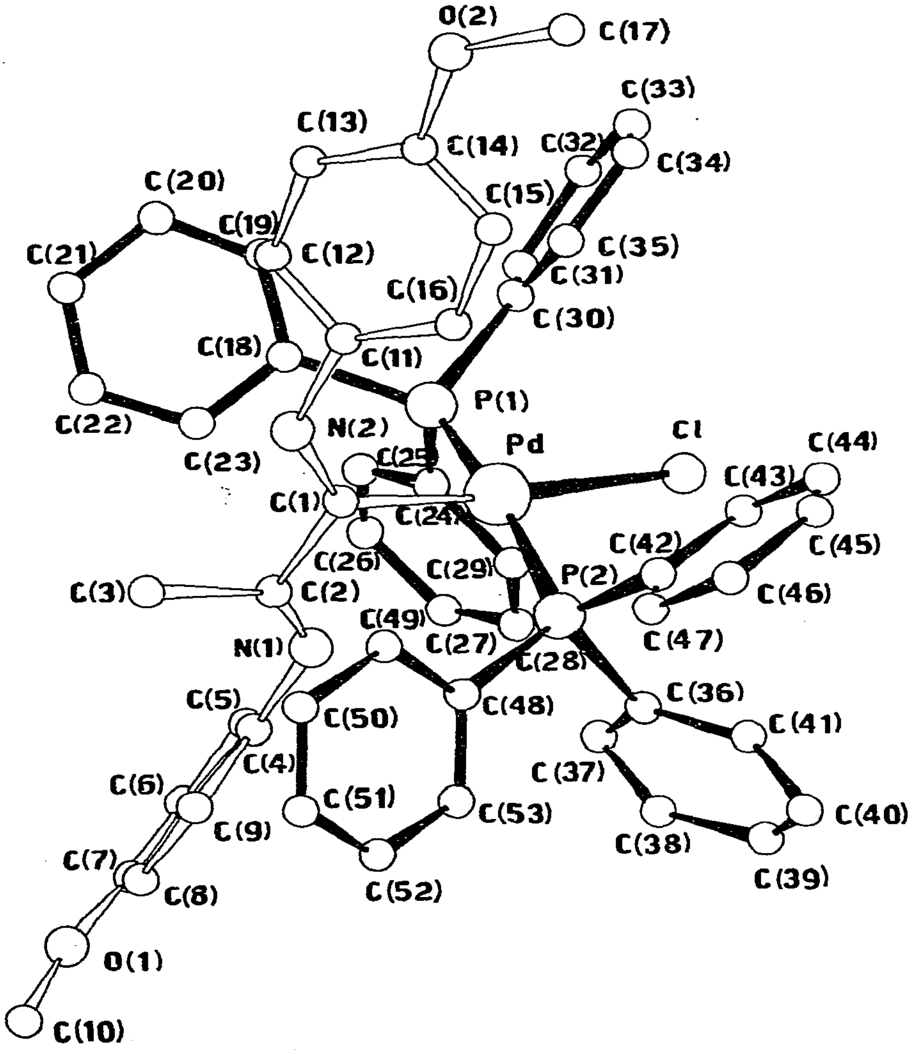

Fig. 1. A perspective view of the complex with the labelling system used in the crystallographic study.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0.2137(1)	0.2199(1)	0.0980(1)	0.031	0.037	0.027	−0.004	−0.001	0.000
Cl	0.1168(3)	0.2413(3)	−0.0581(3)	0.039	0.062	0.034	0.002	−0.005	−0.015
P(1)	0.0818(3)	0.2414(3)	0.2460(3)	0.033	0.036	0.033	−0.003	−0.009	0.000
P(2)	0.3441(3)	0.2384(3)	−0.0508(4)	0.036	0.044	0.038	−0.008	−0.008	0.005

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
O(1)	0.3351(14)	0.6913(14)	0.4488(17)	0.138	C(26)	−0.0498(12)	0.5010(13)	0.3610(17)	0.069
O(2)	0.1535(10)	−0.2186(10)	0.2423(14)	0.100	C(27)	−0.0315(12)	0.5592(12)	0.2551(16)	0.065
N(1)	0.2992(8)	0.3520(9)	0.2374(11)	0.049	C(28)	0.0203(11)	0.5219(11)	0.1481(15)	0.054
N(2)	0.3050(8)	0.1098(8)	0.2889(11)	0.043	C(29)	0.0568(10)	0.4243(10)	0.1458(13)	0.043
C(1)	0.2890(9)	0.1903(10)	0.2311(13)	0.034	C(30)	−0.0134(10)	0.1830(10)	0.2170(13)	0.039
C(2)	0.3261(10)	0.2709(10)	0.2816(13)	0.043	C(31)	−0.1034(12)	0.2221(13)	0.2580(16)	0.066
C(3)	0.3807(12)	0.2470(12)	0.3863(16)	0.063	C(32)	−0.1765(14)	0.1676(15)	0.2390(19)	0.083
C(4)	0.3198(11)	0.4372(12)	0.2842(15)	0.056	C(33)	−0.1521(16)	0.0846(16)	0.1784(20)	0.089
C(5)	0.2421(13)	0.5022(14)	0.3217(18)	0.077	C(34)	−0.0672(14)	0.0473(14)	0.1387(18)	0.075
C(6)	0.2498(15)	0.5849(15)	0.3789(20)	0.087	C(35)	0.0076(12)	0.0950(12)	0.1588(15)	0.059
C(7)	0.3382(16)	0.6023(16)	0.3823(20)	0.093	C(36)	0.3173(9)	0.3467(10)	−0.1398(13)	0.036
C(8)	0.4159(15)	0.5474(15)	0.3423(19)	0.082	C(37)	0.2745(12)	0.4267(12)	−0.0730(15)	0.060
C(9)	0.4097(14)	0.4549(14)	0.2890(18)	0.079	C(38)	0.2536(12)	0.5131(13)	−0.1380(17)	0.065
C(10)	0.4239(25)	0.7100(25)	0.4440(30)	0.165	C(39)	0.2717(13)	0.5184(13)	−0.2678(17)	0.071
C(11)	0.2685(10)	0.0287(10)	0.2663(14)	0.045	C(40)	0.3114(13)	0.4387(13)	−0.3310(17)	0.070
C(12)	0.2364(12)	−0.0263(12)	0.3719(16)	0.060	C(41)	0.3342(12)	0.3522(12)	−0.2650(16)	0.057
C(13)	0.1994(14)	−0.1075(15)	0.3585(19)	0.083	C(42)	0.3778(10)	0.1472(10)	−0.1663(13)	0.042
C(14)	0.1931(12)	−0.1374(12)	0.2438(16)	0.060	C(43)	0.3101(11)	0.1165(11)	−0.2175(14)	0.049
C(15)	0.2276(12)	−0.0872(12)	0.1367(16)	0.059	C(44)	0.3350(12)	0.0509(12)	−0.3119(16)	0.062
C(16)	0.2651(11)	−0.0026(12)	0.1488(15)	0.056	C(45)	0.4253(13)	0.0134(12)	−0.3514(16)	0.065
C(17)	0.1366(17)	−0.2496(17)	0.1281(23)	0.111	C(46)	0.4942(13)	0.0420(13)	−0.2965(17)	0.071
C(18)	0.0874(10)	0.2048(10)	0.4085(13)	0.042	C(47)	0.4721(12)	0.1110(12)	−0.2064(16)	0.062
C(19)	0.0418(11)	0.1324(11)	0.4678(14)	0.051	C(48)	0.4513(11)	0.2545(11)	0.0013(14)	0.049
C(20)	0.0478(12)	0.1057(12)	0.5905(16)	0.061	C(49)	0.4911(11)	0.1784(12)	0.0702(15)	0.055
C(21)	0.0996(11)	0.1557(11)	0.6540(14)	0.050	C(50)	0.5762(12)	0.1894(13)	0.1102(16)	0.066
C(22)	0.1429(10)	0.2291(11)	0.5955(14)	0.045	C(51)	0.6156(11)	0.2718(16)	0.0806(20)	0.091
C(23)	0.1391(10)	0.2574(10)	0.4719(13)	0.043	C(52)	0.5792(15)	0.3449(15)	0.0050(19)	0.083
C(24)	0.0379(9)	0.3663(10)	0.2538(13)	0.037	C(53)	0.4936(12)	0.3352(12)	−0.0346(16)	0.060
C(25)	−0.0150(11)	0.4039(11)	0.3612(15)	0.054					

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) [a]

(a) Bond lengths in the inner coordination sphere

Pd—Cl	2.41(1)	Pd—P(1)	2.33(1)
Pd—C(1)	1.98(1)	Pd—P(2)	2.35(1)

(b) Bond distances within the 1,4-diaza-3-methyl-butadiene-2-yl group

N(1)—C(4)	1.44(2)	C(9)—C(4)	1.41(3)
N(1)—C(2)	1.26(2)	C(7)—O(1)	1.49(3)
C(2)—C(3)	1.52(2)	O(1)—C(10)	1.38(4)
C(2)—C(1)	1.51(2)	C(11)—C(12)	1.41(2)
C(1)—N(2)	1.29(2)	C(12)—C(13)	1.37(3)
N(2)—C(11)	1.40(2)	C(13)—C(14)	1.38(3)
C(4)—C(5)	1.40(2)	C(14)—C(15)	1.40(2)
C(5)—C(6)	1.40(3)	C(15)—C(16)	1.42(3)
C(6)—C(7)	1.38(3)	C(16)—C(11)	1.41(2)
C(7)—C(8)	1.33(3)	C(14)—O(2)	1.37(2)
C(8)—C(9)	1.49(3)	O(2)—C(17)	1.43(3)

(c) Bond distances within the triphenylphosphine ligands

			wtd [b] average for 6 C—C
P(1)—C(18)	1.84(1)	C(18)—C(23)	1.40(1)
P(1)—C(24)	1.81(1)	C(24)—C(29)	1.40(1)
P(1)—C(30)	1.82(2)	C(30)—C(35)	1.40(1)
P(2)—C(36)	1.81(1)	C(36)—C(41)	1.40(1)
P(2)—C(42)	1.83(1)	C(42)—C(47)	1.40(1)
P(2)—C(48)	1.83(2)	C(48)—C(53)	1.41(1)

(d) Selected intermolecular nonbonding distances

Pd ···· N(1)	3.04	Pd ···· C(2)	3.02
Pd ···· N(2)	2.95	Pd ···· C(16)	3.19
P(1) ···· C(1)	3.05	P(2) ···· C(1)	3.13

[a] The numbers in parentheses are esd's in the last significant figure listed. [b] Weighted average (l) of bond lengths, l, are given by the formula $l = \Sigma(l_i/\sigma_i^2)/\Sigma(1/\sigma_i^2)$, where σ_i is the esd derived from the least-squares refinement.

parameter in the last cycle of refinement was 0.5 times its esd and the final ΔF synthesis exhibited no peaks greater than 0.6 e Å^{-3}.

The neutral atomic scattering factors used were those of ref. 10 and the effects of anomalous dispersion of the Pd, Cl and P atoms were included in the calculation of $|F_c|$ [11].

A copy of the list of structure factors may be obtained by application of the authors.

The molecular structure is shown in Fig. 1, which also defines the atom numbering scheme used in the tables. Positional and thermal parameters are reported in Table 2; the bond distances and bond angles are listed in Tables 3 and 4. Details of the mean planes and dihedral angles between planes are given in Table 5.

The calculations were performed on a CDC/CYBER '76 computer (Centro Calcolo Elettronico Interuniversitario Italia Nord-Orientale, Casalecchio-Bologna), using the X-ray system [12].

TABLE 4

SELECTED BOND ANGLES (°)

(a) Angles around the palladium atom			
Cl—Pd—P(1)	88.5(0.2)	P(2)—Pd—Cl	91.0(0.2)
P(1)—Pd—C(1)	89.6(0.4)	P(1)—Pd—P(2)	166.1(0.2)
C(1)—Pd—P(2)	92.1(0.4)	Cl—Pd—C(1)	174.4(0.4)
(b) Angles within the 1,4-diaza-3-methyl-butadiene-2-yl group			
Pd—C(1)—N(2)	127.3(1.2)	C(8)—C(9)—C(4)	114.9(1.6)
Pd—C(1)—C(2)	118.6(1.0)	C(6)—C(7)—O(1)	109.6(1.8)
N(2)—C(1)—C(2)	113.9(1.3)	C(8)—C(7)—O(1)	123.0(2.2)
C(1)—C(2)—C(3)	117.6(1.2)	C(7)—O(1)—C(10)	108.3(2.1)
C(1)—C(2)—N(1)	114.0(1.4)	N(2)—C(11)—C(12)	115.5(1.4)
C(3)—C(2)—N(1)	128.0(1.5)	N(2)—C(11)—C(16)	125.2(1.3)
C(2)—N(1)—C(4)	121.4(1.4)	C(12)—C(11)—C(16)	119.3(1.5)
C(1)—N(2)—C(11)	123.2(1.4)	C(11)—C(12)—C(13)	119.5(1.7)
N(1)—C(4)—C(5)	113.7(1.5)	C(12)—C(13)—C(14)	121.7(1.8)
N(1)—C(4)—C(9)	123.4(1.4)	C(13)—C(14)—C(15)	120.6(1.8)
C(5)—C(4)—C(9)	122.9(1.8)	C(14)—C(15)—C(16)	118.4(1.6)
C(4)—C(5)—C(6)	120.6(1.8)	C(15)—C(16)—C(11)	120.4(1.4)
C(5)—C(6)—C(7)	115.9(1.8)	C(13)—C(14)—O(2)	116.4(1.6)
C(6)—C(7)—C(8)	127.2(2.3)	C(15)—C(14)—O(2)	123.1(1.7)
C(7)—C(8)—C(9)	118.1(2.1)	C(14)—O(2)—C(17)	119.9(1.6)
(c) Angles within the triphenylphosphine ligands			
Pd—P(1)—C(18)	120.0(0.5)	Pd—P(2)—C(36)	107.1(0.4)
Pd—P(1)—C(24)	109.9(0.5)	Pd—P(2)—C(42)	116.7(0.5)
Pd—P(1)—C(30)	115.0(0.5)	Pd—P(2)—C(48)	118.6(0.5)
C(18)—P(1)—C(24)	103.1(0.7)	C(36)—P(2)—C(42)	104.2(0.7)
C(24)—P(1)—C(30)	101.8(0.7)	C(42)—P(2)—C(48)	104.9(0.7)
C(18)—P(1)—C(30)	105.5(0.7)	C(36)—P(2)—C(48)	103.6(0.7)
P(1)—C(18)—C(19)	121.9(1.3)	P(2)—C(36)—C(37)	116.7(1.1)
P(1)—C(18)—C(23)	116.7(1.0)	P(2)—C(36)—C(41)	122.9(1.1)
P(1)—C(24)—C(25)	121.4(1.1)	P(2)—C(42)—C(43)	118.2(1.1)
P(1)—C(24)—C(29)	117.5(1.0)	P(2)—C(42)—C(47)	121.7(1.3)
P(1)—C(30)—C(31)	120.0(1.2)	P(2)—C(48)—C(49)	116.5(1.3)
P(1)—C(30)—C(35)	118.1(1.1)	P(2)—C(48)—C(53)	120.9(1.2

Results and discussion

The crystal structure is composed of discrete molecules of *trans*-[PdCl(dabyl)$(PPh_3)_2$], dabyl = 1,4-bis(*p*-methoxyphenyl)-1,4-diaza-3-methylbutadiene-2-yl group, separated by normal Van der Waals distances. The palladium is four-coordinated and is surrounded in a roughly planar fashion by two *trans* phosphorus atoms of PPh_3 ligands, a chlorine atom, and a σ-bonded carbon atom of dabyl group, as shown in Fig. 1. The inner core of the complex (Fig. 2) exhibits a remarkable distortion from square-planar coordination about Pd(II) towards a tetrahedral arrangement, the four donor atoms being alternately above and below the mean plane (Table 5), and there are some significant deviations of angles between the palladium and its nearest neighbours from their idealized values of 90° or 180° (for example, P(1)—Pd—P(2) angle is only 166.1°) (Table 4). These facts can be primarily attributed to overcrowding caused by the bulky PPh_3 ligands. The Pd—P(1) and Pd—P(2) bond lengths

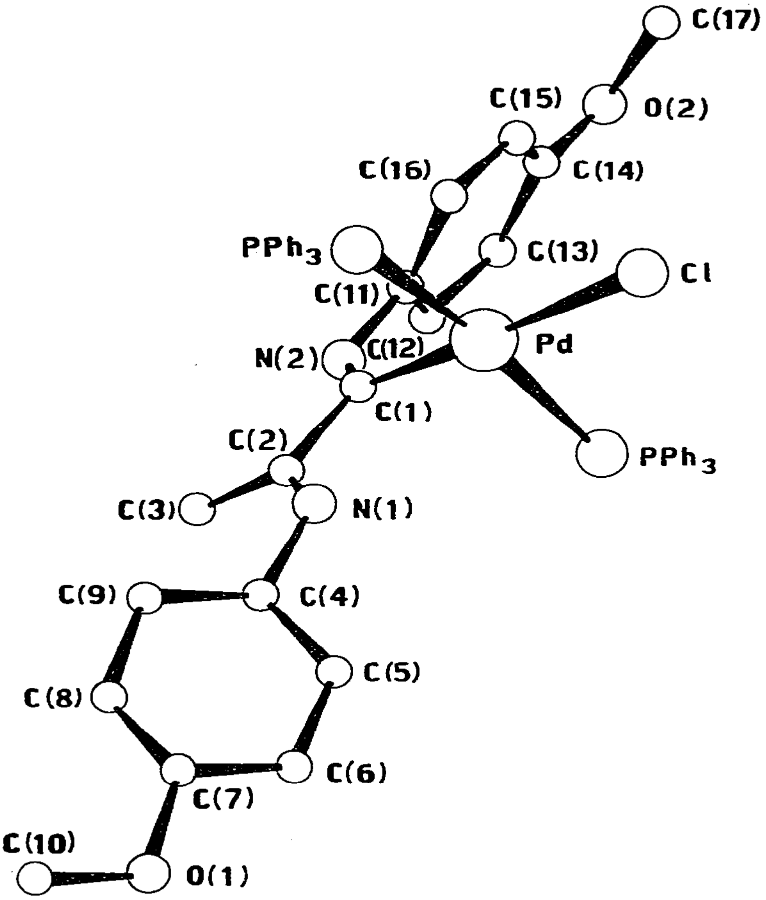

Fig. 2. The inner coordination sphere. The atoms of the phenyl phosphine groups are omitted for clarity.

(2.33(1) and 2.35(1) Å, respectively) are shorter than the single-bond covalent radii sum (2.41 Å) [13], whereas the Pd—Cl bond (2.41(1) Å) is greater than predicted (2.30 Å) (1.31 + 0.99 Å) [13,14]. The Pd—P distances are in accord with the values found in a variety of palladium complexes [15] and the role of π-bonding in the *trans* influence has been reviewed [16]. The lengthening of Pd—Cl bond is mainly due to the "structural" influence [17] of the *trans* ligand (the σ-bonded dabyl group) and accounts for the low value (265 cm^{-1}) of the ν(Pd—Cl) vibration [3]. As can be seen from Table 6, the Pd—Cl bond length falls within the range of Pd—Cl distances observed for palladium complexes containing a chloride ligand *trans* to a Pd—C σ-bond, whereas for the complexes of the type *cis*-[$PdCl_2$(NN)], *cis*-[$PdCl_2$(SS)] and *cis*-[$PdCl_2$(SN)] the Pd—Cl bond lengths vary within the narrow range 2.30—2.33 Å [18].

The geometry of the PPh_3 ligands (Table 3 and 4) agrees quite well with that found in many similar structures and does not call for further comment. The Pd—C(1) length (1.98(1) Å) is somewhat shorter than the sum of covalent radii for a Pd—C(sp^2) bond (1.31 + 0.74 Å) [13], but is consistent with the values observed in other complexes containing a Pd—C(sp^2) σ-bond, as reported in

TABLE 5

LEAST-SQUARES PLANES OF THE FORM $Px + Qy + Rz = S$, WHERE x, y, z ARE FRACTIONAL COORDINATES

Plane no.	Atoms	*P*	*Q*	*R*	*S*
1	Cl, P(1), P(2), C(1)	1.690	14.193	1.383	3.712
2	C(4)—C(9)	0.506	−5.923	9.684	0.303
3	C(11)—C(16)	12.583	−5.837	1.032	3.501
4	C(18)—C(23)	10.325	−7.919	−2.124	−1.600
5	C(24)—C(29)	13.837	4.967	5.063	3.629
6	C(30)—C(35)	1.731	−6.187	9.588	0.931
7	C(36)—C(41)	14.402	5.472	2.280	6.137
8	C(42)—C(47)	1.042	10.182	−7.115	3.074
9	C(48)—C(53)	−4.748	5.862	8.592	−0.666
10	N(2)—C(1)—C(2)—N(1)	10.614	−1.047	−6.101	1.409

Distances (Å) of atoms from the planes [a]

Plane no.	
1	Cl, −0.17; P(1), 0.19; P(2), 0.18; C(1), −0.20; [Pd], −0.09; [N(1)], 2.12; [N(2)], −1.24; [C(2)], 1.07; [C(3)], 0.97
2	[N(1)], 0.06; [C(2)], 0.98; [O(1)], 0.12; [C(10)], 0.01; [Pd], −0.55
3	[N(2)], 0.01; [C(1)], −0.74; [C(2)], −0.04; [C(17)], −0.19; [Pd], −1.99
10	N(2), −0.05; C(1), 0.05; C(2), 0.05; N(1), −0.05; [Pd], 0.03; [Cl], −0.07; [C(3)], 0.02; [C(11)], −0.21; [C(4)], −0.21

Dihedral angles (°) between planes

1—2	69.0	2—10	59.0	4—6	82.7
1—3	64.2	3—10	44.3	7—8	77.0
1—10	82.1	4—5	65.6	8—9	74.2
2—3	76.8	5—6	74.5	7—9	80.4

[a] Atoms not included in the least-squares plane calculation are in brackets.

Table 6. In Table 6 some representative Pd—C(sp^3) bond-distances are also listed in order to show the lengthening of Pd—C with the change of hybridization at the carbon atom. There appears, therefore, to be little, if any, π-bonding interaction between palladium and the σ-bonded dabyl group. This structural result alone does not account for the stability of the Pd—C bond towards electrophilic cleavage [3] and the inertness of the Pd—C=N group towards acid catalyzed hydrolysis [7]. This behaviour is to be ascribed either to steric hindrance of the *trans* phosphine ligands or to electronic stabilization resulting from monoprotonation of dabyl group. The nitrogen atoms of this group, at 2.95(2) and 3.04(2) Å away from palladium, are clearly not bonded to the metal in this molecular structure, as had been suggested previously for the closely related compound $[PdI\{C(=NC_6H_{11})C(Me)=NC_6H_{11}\}(PMe_2Ph)_2]$ [19]. Thus the sterically hindered rotation around the Pd—C bond seems to be the most reasonable explanation for the magnetical non-equivalence of the phosphine-methyl groups in the latter complex.

As can be seen from the Figures, the σ-bonded dabyl group assumes a *trans* configuration with *anti* p-C_6H_4—OMe N-substituents. The N=C—C=N fragment is virtually planar, and its mean plane is nearly normal (82.1°) to the mean coordination plane. The carbon—nitrogen bond lengths are of two types:

TABLE 6

DISTANCES (Å) IN SOME MONOMERIC PALLADIUM(II)—CARBON σ-BONDED COMPLEXES

	Pd—C	Pd—P	Pd—Cl [e]	Ref.
$[PdCl_2(Me_2C_2N_4H_4)]$	1.95		2.39	25
$[Pd(NCS)(o\text{-}CCC_6H_4CCH)(PEt_3)_2]$	1.95	2.32		26
$[PdCl_2(MeHNCOCH_3)_2]$	1.96		2.37	27
$[PdCl(COCO_2CH_3)(PPh_3)_2]$	1.97	2.32	2.43	28
$[FdCl(MDAP)(NH_2CH(Me)Ph)]$ [a]	1.97		2.45	29
$[PdCl\{\overline{C(N\text{-}p\text{-}C_6H_4OMe)C}(Me)N\text{-}p\text{-}C_6H_4OMe\}(PPh_3)_2]$	1.98	2.34	2.41	[f]
$[(n\text{-}Bu)_4N]^+[PdClBr(C{-}N)]$ [b]	1.98			30
$[Pd(dmba)(salNPh)]$ [c]	1.98			31
$[PdCl(Azb)(PEt_3)_2]$ [d]	1.99	2.31	2.38	32
$[PdBr\{C_4(COOMe)_4H\}(PPh_3)_2]$	1.99	2.35		33
$[Pd\{OC(Me)CH(COMe)C(CF_3)C(CF_3)\}_2]$	1.99			34
$[Pd(acac)(C_4Ph_4OEt)(PMe_2Ph)]$	2.00	2.23		35
$[Pd\{OC(Me)CH(COMe)C(CF_3)C(CF_3)\}\{NMe_2CH_2C_6H_4\}]$	2.00			34
$[PdCl(C{-}N)(PEt_3)_2]$ [b]	2.01	2.32	2.41	30
$[Pd(acac)\{C_5Me_5CH(p\text{-}tolyl)CH_2\}]$	2.02			36
$[Pd\{(C_5H_5)(CH_2CH(OH)(CH_2)_2CHCH(CH_2)_2\}]$	2.03			37
$[Pd(C_2H_2O_2)(py)(PPh_3)]$	2.03	2.23		38
$[PdCl\{HC_8(CO_2Me)_8\}(py)_2]$	2.04		2.51	39
$[PdCl(CH_2COCH_2COOCH_2Ph)(py)_2]$	2.05			40
$[PdCl(CH\text{-}t\text{-}BuCHCHC(Cl)\text{-}t\text{-}Bu)(MesSCH_2CH_2SMe)]$	2.06			41
$[Pd(acac)_2(PPh_3)\cdot 0.5\ C_6H_6]$	2.11	2.26		42
$[PdBr(C_7H_8OMe)(py)_2]$	2.16			43

[a] MDAP = (2-methoxy-3-*N,N*-dimethylaminopropyl-C^1,*N*). [b] C—N=N—(phenylamino)-α-methylbenzylidenimino-2-*C,N*; [c] dmba = *N,N*-dimethylbenzylamine; salNPh = *N*-phenylsalicylaldimine. [d] Azb = 2-(phenylazo)phenyl. [e] In *trans* position to a Pd—C bond. [f] Present work.

(i) C(ph)—N 1.44(3) and 1.40(3) Å; (ii) N=C 1.26(2) and 1.29(2) Å, while the C(1)—C(2) bond is 1.51(2) Å.

From a structural point of view this corresponds to two C=N groups joined by a single $C(sp^2)$—$C(sp^2)$ bond. However, the planarity of the diazabutadiene moiety implies the presence of π-electron delocalization over the four atoms of the conjugated double-bond system, in the same way as reported for the *trans* planar 1,3-butadiene molecule, for which the following distances have been determined: C=C 1.34(1) and C—C 1.48(1) Å [20]. The slightly longer C(1)—C(2) bond and the shorter C=N bonds in the dabyl group are probably related to the higher electronegativity of the nitrogen atoms.

The phenyl rings of the N-substituents do not interact with the π-system of the diazabutadiene moiety, as they are rotated by 59° and 44° out of the N=C—C=N plane, and form each other a dihedral angle of 76.8° (Table 5).

The remaining average bonding parameters of the dabyl ligand agree satisfactorily with the accepted values [13], even though the methoxy groups, being the most flexible moieties, experience high thermal motion and/or disorder and hence bond distances and angles in these portions of the complex are not representative.

It is likely that the dabyl group retains its *trans* configuration in the other organometallic Pd^{II}-1,4-diazabutadienes, which can be prepared from [PdCl(dabyl)$(PPh_3)_2$] either by substitution reaction at the Pd centre or by change of substituents at the imino atoms [3—7]. This would agree with the ^1H NMR results, which indicate that in this class of derivatives in solution the σ-bonded 1,4-diaza-3-methylbutadiene-2-yl ligand assumes only one of its possible configurations.

The molecular structure accounts also for some typical features of the ^1H NMR spectrum of [PdCl(dabyl)$(PPh_3)_2$] in $CDCl_3$ [3]. Thus, the down-field shift of the *ortho* protons of the p-C_6H_4OMe group at position 1 on the diazabutadiene chain results from the deshielding effect of the palladium atom in close proximity (Pd—C(16) = 3.19 Å, with a calculated Pd—H distance of 2.69 Å, by assuming an H—C(16) bond length of 1.08 Å) [21,22]. On the other hand, the resonance of the methyl group at position 3 is shifted up-field [δ(C—Me) 1.29 ppm] relative to the corresponding signal of the organic diazabutadiene R—N=C(Me)—C(Me)=N—R (R = p-C_6H_4OMe) [δ(C—Me) 2.10 ppm] [23]. This is mainly due to the shielding effect of the phenyl ring current of the two mutually *trans* PPh_3 ligands, as can be inferred from the relative position of the methyl group, indicated by C(3) in Fig. 1.

This is further supported (i) by the down-field shift trend of δ(C—Me) upon progressive substitution of phenyl by methyl groups in the phosphine ligands of the closely related series of complexes, *trans*-$[PdI\{\overline{C(=NC_6H_{11})C}(Me)=NC_6H_{11}\}(PMe_xPh_{3-x})_2]$: $x = 0$, δ 1.19; $x = 1$, δ 1.57; $x = 2$, δ 2.04; $x = 3$, δ 2.34 ppm [19]; and (ii) by the down-field shift of δ(C—Me) in the following compounds having only one phosphine ligand *cis* to the dabyl group: [PdCl(dabyl)(diphos)], δ 1.88 [4]; [Pd(dmtc)(dabyl)(PPh_3)] δ 1.87 [24]; [Pd(acac)(dabyl)(PPh_3)] δ 1.88 or 1.83 ppm [23].

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