Crystal and Molecular Structure of 4-[(Diethylamino)(t-butylamino)-methylene]-4-(t-butyl isocyanide)-2,2,5,5-tetrakis(trifluoromethyl)-1,3,4-dioxapalladolan: A Palladium(II) Carbene Complex

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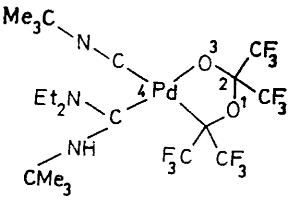
Crystals of the title compound (I) are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions: $a = 20{\cdot}093(3)$, $b = 9{\cdot}519(2)$, $c = 15{\cdot}201(3)$ Å, $\beta = 96{\cdot}77(2)°$. The structure has been elucidated by conventional heavy-atom methods from 4123 diffracted intensities measured on a four-circle diffractometer, and refined to R 0·099. The palladium atom, which is in an approximately square-planar environment, forms part of a five-membered condensed hexafluoroacetone ring, $\overline{\mathrm{Pd{\cdot}C(CF_3)_2O{\cdot}C(CF_3)_2O}}$, which is of envelope conformation. The $O-C(CF_3)_2$ bond from the oxygen atom adjacent to the metal in this ring is notably short [1·337(13) Å]. The plane of the carbene ligand lies perpendicular to the co-ordination plane of the Pd atom; there is virtually no back-donation from Pd to carbene [Pd–C(4) 2·07 Å], and the carbene lies *trans* to C(1) of the five-membered ring. The C–N bond distances within the carbenoid fragment (mean 1·32 Å) indicate a high degree of delocalisation. The short intramolecular contact between the H atom of the $NHBu^t$ group and one of the methylene hydrogen atoms of the NEt_2 group supports spectroscopic evidence for restricted rotation around an N–Et bond.

THE overall configuration of the title compound (I) had already been established by spectroscopic studies.[1] A detailed interpretation of the ^1H n.m.r. spectrum led to the suggestion that there must be restricted rotation about one of the N–Et bonds caused by steric interaction between one of the methylene H atoms of the Et group and the N*H* atom of the carbene ligand. It was also assumed (by inference from previous *X*-ray studies) [2] that the N–C–N plane of the carbene would lie perpendicular to the plane of the five-membered ring. To establish these points, and to obtain further information on the details of the structure, this *X*-ray determination was undertaken.



(I) showing the systematic numbering

EXPERIMENTAL

Crystals of (I) grow as colourless prisms elongated in the *a* direction. The dimensions of the one chosen for *X*-ray diffraction were 0·35 × 0·30 × 0·12 mm; this crystal was mounted on a Syntex $P2_1$ four-circle diffractometer under the control of a Nova 1200 computer.[3] Lattice parameters were determined by refinement of the x and y co-ordinates of 15 reflections chosen from a 15-minute rotation photograph taken (on the diffractometer) with a Polaroid film cassette mounted 97·5 mm from the crystal, with 2θ, ω, and χ all at 0°. The shortest three independent reciprocal vectors were used by the auto-indexing routine to generate, by linear combinations, other real-space vectors as possible unit-cell axes. Only those combinations which produced near-integer values for the indices

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[1] C. H. Davies, C. H. Game, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 357.

[2] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487, and refs. therein.

[3] R. A. Sparkes, 'SYNTEX $P2_1$ Operations Manual,' Syntex Analytical Instruments, Cupertino, U.S.A., 1973.

to the other 12 planes were output, with the cosines of the angles between all such axes. The unit cell was then defined by inspection. The setting angles for the 15 reflections were used to calculate the cell dimensions, their standard deviations, and the orientation matrix, by least-squares refinement. A number of intensities for which $30° \leqslant 2\theta \leqslant 36°$ were rapidly measured by use of this matrix; 15 of these were chosen and recentred to obtain more accurate cell parameters. Intensities were measured with Mo-K_α radiation and a graphite monochromator. A preliminary peak count for 2·5 s was used to determine the scan rate. Sample counts of >600 were subsequently measured at the fastest scan speed (0·997° s^{-1}), while those <20 were measured at 0·0337° s^{-1}; intermediate values were measured at appropriate submultiples of the fastest rate. A θ—2θ scan in 96 steps with bisecting geometry was used; backgrounds were measured before and after each scan, so that the total background time was equal to the scan time. The range of 2θ was from 1° below the Bragg angle for Mo-$K_{\alpha1}$ to 1° above the angle for Mo-$K_{\alpha2}$. A linear correction for counter coincidence effects was made for each intensity step for which the count exceeded 5000. (For counts exceeding 50,000 this correction is considered invalid and the reflection flagged for re-investigation; no such reflections occurred for the crystal under study.) Five reflections were remeasured between every 55 measured intensities in order to check the stability of the apparatus and of the crystal. The check reflections were analysed by the program DRSYN on the local ICL 4/75 computer.[4] Reflections for which $I < 2{\cdot}5\sigma(I)$ were regarded as 'unobserved' for the purposes of structure solution, but were included in the final stages of the refinement. Of the total 5118 independent reflections (complete for $3{\cdot}7° \leqslant 2\theta \leqslant 50{\cdot}0°$), 2344 were unobserved. Weighted and unweighted least-squares plots of (I) and of $\ln(I)$ *vs.* exposure time for the 5 check reflections showed insignificant time dependence: overall changes in intensity varied between -8% and 2% over the 174 h crystal exposure time. The 103 measurements of each reference reflection gave standard deviations 1·1—1·8 times those derived from counting statistics, indicating reasonable constancy. Of the 342 systematic absences measured, 7 were above the 2·5σ threshold, and for 13 others the value of I/σ fell below $-2{\cdot}5$, the ratio $I:\sigma$ ranging from $-4{\cdot}6$ to 4·1.

TABLE 1

Atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$10^2U/\text{Å}^2$ *
Five-membered ring				
Pd	0·51441(3)	0·38179(7)	0·25161(5)	†
O(1)	0·5883(3)	0·4820(7)	0·3272(4)	†
C(2)	0·6465(5)	0·4847(12)	0·2927(7)	8·2(3)
O(2)	0·6537(3)	0·3924(9)	0·2220(5)	†
C(1)	0·5940(5)	0·3192(10)	0·1849(6)	7·4(3)
C(11)	0·5867(6)	0·3530(14)	0·0883(8)	9·4(3)
F(111)	0·6426(3)	0·3410(11)	0·0489(5)	†
F(112)	0·5674(4)	0·4831(10)	0·0723(5)	†
F(113)	0·5407(4)	0·2744(10)	0·0408(5)	†
C(12)	0·6088(6)	0·1651(13)	0·2008(8)	9·0(3)
F(121)	0·6648(3)	0·1213(9)	0·1676(6)	†
F(122)	0·5608(4)	0·0828(7)	0·1638(6)	†
F(123)	0·6182(4)	0·1349(9)	0·2857(6)	†
C(21)	0·7030(9)	0·4519(22)	0·3639(13)	13·7(6)
F(211)	0·7633(4)	0·4582(21)	0·3366(8)	†
F(212)	0·6961(6)	0·3251(15)	0·3941(7)	†
F(213)	0·7044(4)	0·5264(15)	0·4378(6)	†
C(22)	0·6598(8)	0·6336(19)	0·2566(11)	12·0(4)
F(221)	0·7115(6)	0·6457(13)	0·2151(8)	†
F(222)	0·6084(7)	0·6759(10)	0·2020(8)	†
F(223)	0·6640(6)	0·7313(11)	0·3218(7)	†
Isocyanide ligand				
C(3)	0·4464(5)	0·2908(10)	0·1758(6)	6·6(2)
N(3)	0·4031(4)	0·2413(8)	0·1300(5)	7·2(2)
C(30)	0·3499(6)	0·1705(12)	0·0700(7)	8·7(3)
C(31)	0·3038(8)	0·2917(19)	0·0316(13)	†
C(32)	0·3833(9)	0·1035(27)	−0·0010(13)	†
C(33)	0·3113(8)	0·0782(20)	0·1279(12)	†
Carbene ligand				
C(4)	0·4387(4)	0·4448(10)	0·3246(6)	6·3(2)
N(4)	0·4216(4)	0·3759(9)	0·3918(5)	7·1(2)
H(400)	0·3829	0·4154	0·4180	8·0
C(40)	0·4510(5)	0·2467(10)	0·4360(6)	7·1(2)
C(41)	0·4470(7)	0·1227(12)	0·3715(8)	†
C(42)	0·5235(6)	0·2773(14)	0·4761(9)	†
C(43)	0·4076(7)	0·2141(16)	0·5113(9)	†
N(5)	0·4044(4)	0·5616(9)	0·3005(6)	8·0(2)
C(51)	0·4202(7)	0·6483(13)	0·2259(11)	†
H(511)	0·4490	0·5860	0·1856	8·0
H(512)	0·3740	0·6781	0·1881	8·0
C(52)	0·4585(11)	0·7777(19)	0·2514(16)	†
C(61)	0·3457(6)	0·6090(12)	0·3443(9)	†
H(611)	0·3563	0·5945	0·4143	8·0
H(612)	0·3365	0·7179	0·3302	8·0
C(62)	0·2830(6)	0·5238(17)	0·3100(13)	†

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$, with parameters ($\times 10^2$):

TABLE 1 (*Continued*)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	5·03(7)	6·16(8)	7·22(8)	0·15(3)	0·48(3)	−0·90(4)
O(1)	5·7(3)	9·1(5)	8·6(4)	−1·0(3)	1·3(3)	−2·5(4)
O(2)	5·1(3)	13·3(6)	9·8(5)	−1·5(4)	1·4(3)	−4·3(5)
F(111)	8·6(4)	24·0(10)	10·2(5)	−1·5(5)	4·1(4)	−2·6(6)
F(112)	13·5(6)	14·9(7)	10·8(5)	−0·6(5)	1·6(4)	2·2(5)
F(113)	10·3(5)	19·7(8)	8·8(4)	−4·7(5)	0·8(4)	−4·2(5)
F(121)	9·0(4)	14·6(6)	16·7(7)	4·2(5)	3·1(4)	−4·7(6)
F(122)	10·2(5)	8·9(5)	19·4(8)	0·4(4)	1·8(5)	−4·2(5)
F(123)	14·5(6)	11·8(6)	14·1(6)	5·9(5)	2·1(5)	1·9(5)
F(211)	6·0(4)	55·1(28)	18·4(9)	−0·1(9)	0·7(5)	−13·9(14)
F(212)	17·2(9)	24·8(14)	13·2(7)	7·9(9)	−5·7(6)	−1·7(8)
F(213)	11·4(6)	31·4(15)	13·7(7)	1·6(7)	−2·6(5)	−11·7(9)
F(221)	21·7(10)	21·9(11)	21·2(10)	−11·8(9)	14·7(9)	−9·7(9)
F(222)	23·8(12)	10·7(6)	19·0(10)	−2·2(7)	4·7(9)	2·2(6)
F(223)	23·9(11)	16·7(8)	18·6(9)	−12·0(8)	11·8(8)	−9·8(8)
C(31)	10·6(10)	14·8(14)	19·2(16)	−1·5(10)	−5·2(11)	4·0(13)
C(32)	13·4(13)	28·0(27)	17·8(16)	−0·7(15)	1·6(11)	−15·9(18)
C(33)	13·6(12)	17·7(17)	14·9(13)	−8·4(12)	−1·0(10)	3·9(12)
C(41)	14·1(10)	5·9(6)	9·6(8)	1·1(7)	1·0(7)	−0·4(6)
C(42)	8·7(8)	9·4(8)	12·4(10)	−0·6(6)	−1·5(7)	2·4(7)
C(43)	12·2(10)	12·4(11)	9·6(8)	−0·7(8)	3·6(7)	1·5(8)
C(51)	11·7(10)	7·8(8)	15·5(12)	2·4(7)	1·4(9)	0·6(8)
C(52)	21·1(20)	10·0(12)	22·4(21)	−2·9(13)	−0·5(16)	0·7(13)
C(61)	8·5(7)	7·5(7)	15·0(10)	3·6(6)	2·0(7)	−1·8(7)
C(62)	6·1(7)	12·3(11)	24·2(19)	0·6(7)	−0·3(9)	−3·5(12)

RESULTS

Crystal Data.—$C_{20}H_{29}F_{12}N_3O_2Pd$, $M = 677{\cdot}9$. Monoclinic, $a = 20{\cdot}093(3)$, $b = 9{\cdot}519(2)$, $c = 15{\cdot}201(3)$ Å, $\beta = 96{\cdot}77(2)°$, $Z = 4$, $D_c = 1{\cdot}56$ g cm^{-3}, $D_m = 1{\cdot}51$, $F(000) = 1360$. Space group $P2_1/a$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo-}K_\alpha) = 7{\cdot}38$ cm^{-1}.

The probable position of the Pd atom was apparent from pseudoabsences for hkl: $2h + k = 4n + 2$, and $h + k + l = 2n + 1$. The resulting approximate co-ordinates $(\frac{1}{2}, \frac{3}{8}, \frac{1}{4})$ were confirmed by Patterson synthesis, and the remainder of the structure was elucidated by electron-density difference syntheses. Subsequent structure refinement by full-matrix least squares, using 2774 'observed' reflections and with isotropic thermal parameters for all atoms except Pd, led to R 0·106 (R' 0·113). Further

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances	
Five-membered ring	
Pd–O(1)	2·008(6)
O(1)–C(2)	1·337(13)
C(2)–O(2)	1·409(14)
O(2)–C(1)	1·444(11)
C(1)–Pd	2·080(10)
C(1)–C(11)	1·493(15)
C(11)–F(111)	1·338(15)
C(11)–F(112)	1·311(16)
C(11)–F(113)	1·333(14)
C(1)–C(12)	1·511(16)
C(12)–F(121)	1·353(15)
C(12)–F(122)	1·316(14)
C(12)–F(123)	1·315(15)
C(2)–C(21)	1·506(21)
C(21)–F(211)	1·327(22)
C(21)–F(212)	1·305(25)
C(21)–F(213)	1·326(23)
C(2)–C(22)	1·555(21)
C(22)–F(221)	1·283(21)
C(22)–F(222)	1·309(19)
C(22)–F(223)	1·354(20)
Isocyanide ligand	
Pd–C(3)	1·891(9)
C(3)–N(3)	1·149(11)
N(3)–C(30)	1·482(13)
C(30)–C(31)	1·551(20)
C(30)–C(32)	1·480(24)
C(30)–C(33)	1·520(22)
Carbene ligand	
Pd–C(4)	2·074(9)
C(4)–N(4)	1·294(12)
N(4)–C(40)	1·490(13)
C(40)–C(41)	1·531(15)
C(40)–C(42)	1·539(15)
C(40)–C(43)	1·550(17)
C(4)–N(5)	1·337(12)
N(5)–C(51)	1·467(18)
C(51)–C(52)	1·479(23)
N(5)–C(62)	1·491(15)
C(61)–C(62)	1·535(18)
(*b*) Angles	
Five-membered ring	
C(1)–Pd–O(1)	81·7(3)
Pd–O(1)–C(2)	114·0(6)
O(1)–C(2)–O(2)	117·5(8)
C(2)–O(2)–C(1)	116·3(7)
O(2)–C(1)–Pd	108·8(6)
Pd–C(1)–C(11)	115·2(7)
Pd–C(1)–C(12)	110·3(7)
O(2)–C(1)–C(11)	105·2(8)
O(2)–C(1)–C(12)	105·5(8)
C(11)–C(1)–C(12)	111·2(9)
O(1)–C(2)–C(21)	109·6(11)
O(1)–C(2)–C(22)	110·5(10)
O(2)–C(2)–C(21)	106·4(11)
O(2)–C(2)–C(22)	105·2(10)
C(21)–C(2)–C(22)	107·2(12)
C(1)–C(11)–F(111)	115·5(9)
C(1)–C(11)–F(112)	112·2(10)
C(1)–C(11)–F(113)	113·2(10)
F(111)–C(11)–F(112)	104·1(11)
F(111)–C(11)–F(113)	105·9(10)
F(112)–C(11)–F(113)	105·0(10)
C(1)–C(12)–F(121)	113·3(10)
C(1)–C(12)–F(122)	112·9(9)
C(1)–C(12)–F(123)	111·8(10)
F(121)–C(12)–F(122)	105·0(10)
F(121)–C(12)–F(123)	105·6(9)
F(122)–C(12)–F(123)	107·6(10)
C(2)–C(21)–F(211)	113·9(15)
C(2)–C(21)–F(212)	110·0(14)
C(2)–C(21)–F(213)	115·9(15)
F(211)–C(21)–F(212)	106·9(17)
F(211)–C(21)–F(213)	108·2(15)
F(212)–C(21)–F(213)	100·9(15)
C(2)–C(22)–F(221)	116·0(14)
C(2)–C(22)–F(222)	110·5(12)
C(2)–C(22)–F(223)	111·5(12)
F(221)–C(22)–F(222)	106·5(14)
F(221)–C(22)–F(223)	108·3(14)
F(222)–C(22)–F(223)	103·3(13)
Isocyanide ligand	
Pd–C(3)–N(3)	176·6(8)
C(3)–N(3)–C(30)	176·7(10)
N(3)–C(30)–C(31)	104·4(10)
N(3)–C(30)–C(32)	106·8(10)
N(3)–C(30)–C(33)	106·7(10)
C(31)–C(30)–C(32)	110·3(13)
C(31)–C(30)–C(33)	109·0(12)
C(32)–C(30)–C(33)	118·7(14)
Carbene ligand	
Pd–C(4)–N(4)	123·8(7)
Pd–C(4)–N(5)	118·7(7)
N(4)–C(4)–N(5)	117·5(9)
C(4)–N(4)–C(40)	130·3(8)
N(4)–C(40)–C(41)	111·1(8)
N(4)–C(40)–C(42)	109·1(8)
N(4)–C(40)–C(43)	105·7(8)
C(41)–C(40)–C(42)	112·0(9)
C(41)–C(40)–C(43)	109·1(9)
C(42)–C(40)–C(43)	109·5(9)
C(4)–N(5)–C(51)	121·9(9)
C(4)–N(5)–C(61)	122·6(9)
C(51)–N(5)–C(61)	115·4(9)
N(5)–C(51)–C(52)	114·8(14)
N(5)–C(61)–C(62)	110·4(11)
Co-ordination around Pd	
C(1)–Pd–C(3)	96·5(4)
C(1)–Pd–C(4)	176·8(5)
O(1)–Pd–C(4)	95·5(3)
O(1)–Pd–C(3)	177·4(7)
C(3)–Pd–C(4)	86·3(4)

refinement allowed anisotropic thermal parameters for the O, F, and terminal methyl and ethyl C atoms as well as for the Pd atom, but with so large a matrix it was necessary to define two blocks comprising (i) the Pd atom and all the atoms of the five-membered ring, scale factor, and overall temperature factor, and (ii) the two chain ligands. Hydrogen atoms (except those in methyl groups) were incorporated at calculated positions (C–H 1·08, N–H 0·99 Å) with U 0·08 Å^2 and were not refined, but three reflections with large $|F_0|$ were deleted (0,0,2, 2,0,$\bar{1}$, and 2,0,2). Weights were applied according to $1/w = a + b|F| + c|F|^{-1}$, with $a = -10$, $b = 0{\cdot}3$, and $c = 164$; convergence was obtained at R 0·059 (R' 0·075). Finally, unobserved reflections for which $F_o < |F_c|$ were introduced into the refinement. A new weighting scheme[8] $1/w = x\,.\,y$, where $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta \geqslant b$, and $y = F/a$ if $F > a$, $y = 1$ if $F \leqslant a$ ($a = 100$, $b = 0{\cdot}31$) in which unobserved reflections were weighted by 0·36 times the calculated weight, led to R 0·099 (for 4123 data including 1352 unobserved reflections). For the observed reflections only, the new agreement indices were R 0·061, R' 0·069. In the final difference synthesis the largest peaks (*ca.* 0·6 eÅ^{-3}) were in the region of the Pd, C(22), and the C(51) atoms, and in the last cycle the mean shift-to-error was 0·11.

Positional and thermal parameters are in Table 1, interatomic distances in Table 2, and some least-squares planes in Table 3. No absorption correction was applied, and the atomic scattering factors were the analytic types of ref. 5 for palladium (corrected for anomalous dispersion),[6] fluorine, oxygen, nitrogen, and carbon, and those of ref. 7 for hydrogen. All computational work was carried out (on the CDC 7600 of the University of London) by use of the *X*-Ray system of programs.[8] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21086 (30 pp., 1 microfiche).*

TABLE 3

(*a*) Equations of some least-squares planes: distances (Å) of relevant atoms from these planes are given in square brackets

(i) Five-membered ring

Plane (1): Pd, O(1), C(2), O(2), C(1)

$$2{\cdot}8761x - 7{\cdot}4301y + 8{\cdot}9279z = 0{\cdot}9453$$

[Pd −0·056, O(1) 0·087, C(2) −0·074, O(2) 0·001, C(1) 0·042]

Plane (2): Pd, C(2), O(2), C(1)

$$2{\cdot}5667x - 7{\cdot}1018y + 9{\cdot}6352z = 1{\cdot}0350$$

[Pd −0·002, O(1) 0·205, C(2) 0·003, O(2) −0·005, C(1) 0·004]

Plane (3): C(1), C(11), C(12)

$$19{\cdot}6961x + 1{\cdot}7954y - 0{\cdot}8609z = 12{\cdot}1138$$

Plane (4): C(2), C(21), C(22)

$$12{\cdot}1527x - 3{\cdot}8580y - 11{\cdot}4305z = 2{\cdot}6406$$

(ii) Carbene ligand

Plane (5): Pd, C(40), N(4), C(4), N(5), C(51), C(61)

$$11{\cdot}5351x + 5{\cdot}2050y + 8{\cdot}1710z = 10{\cdot}0222$$

[Pd −0·045, C(40) 0·027, N(4) 0·000, C(4) 0·007, N(5) 0·020, C(51) 0·044, C(61) −0·052]

Plane (6): N(4), C(4), N(5)

$$11{\cdot}6297x + 5{\cdot}1221y + 8{\cdot}2123z = 10{\cdot}0468$$

[Pd −0·043, C(40) 0·042, C(51) 0·015, C(61) −0·081]

(iii) Co-ordination plane around Pd

Plane (7): Pd, O(1), C(1), C(3), C(4)

$$1{\cdot}3850x - 7{\cdot}7766y + 8{\cdot}5186z = -0{\cdot}1153$$

[Pd 0·002, O(1) −0·031, C(1) 0·030, C(3) −0·031, C(4) 0·029]

(*b*) Angles (°) between least-squares planes

(1)–(3)	88·3	(1)–(4)	89·2	(1)–(5)	88·5
(5)–(7)	86·7	(2)–(7)	7·0		

DISCUSSION

Our results show that (I) contains a nearly planar five-membered $\overline{\mathrm{Pd{\cdot}C(CF_3)_2O{\cdot}C(CF_3)_2O}}$ ring with two other ligands CNBu^t and [C(NEt$_2$)NHBu^t] on the

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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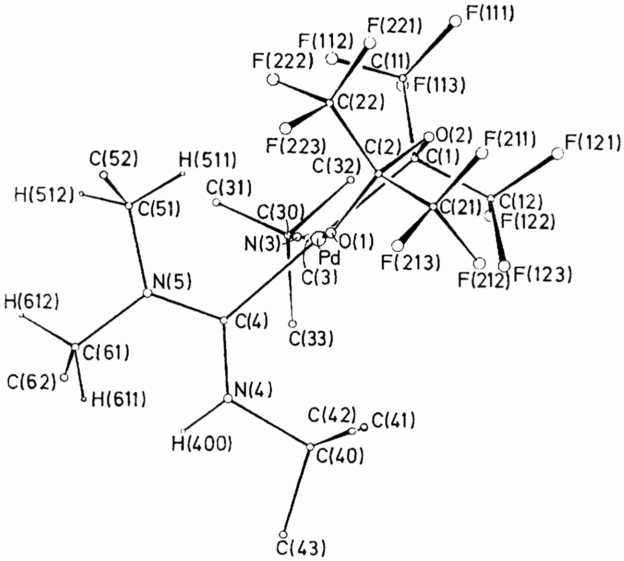

FIGURE 1 View of molecule normal to the plane of the carbene ligand, showing atom numbering

palladium; this gives the palladium an approximately square-planar configuration. The carbene N–C–N plane is, as expected, approximately perpendicular to the co-ordination plane of the metal atom. Figure 1 shows the molecule viewed perpendicular to the plane of the carbene fragment; it also gives the atom numbering sequence used in the crystallographic analysis. There are no abnormally short intermolecular contacts: Figure 2 shows the packing of the molecules. Several portions of the molecule possess detailed features of peculiar interest and will be considered in turn.

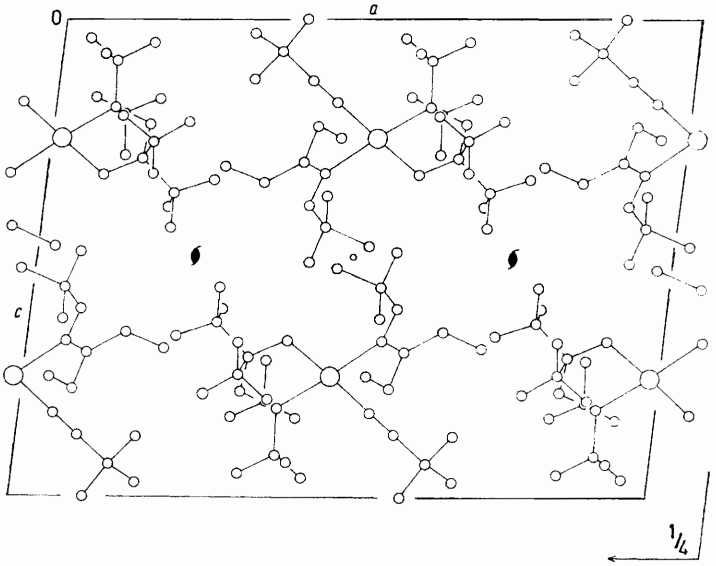

FIGURE 2 Arrangement of molecules in the unit cell, viewed down *b*, looking towards the origin

Five-membered Ring. The Pd–C(1) distance [2·080(11) Å] is close to the sum of the covalent radii for palladium(II) (1·31 Å) and for C(*sp*³) (0·77 Å);[9] the structure determination reveals that this bond lies *trans* to the carbene ligand. The adjacent C(1)–O(2) bond [1·444(11) Å] is rather longer than its next neighbour O(2)–C(2) [1·409(14) Å]. The sum of the radii would suggest a bond length of 1·43 Å here, and neither bond differs significantly from this. The next bond, C(2)–O(1), however, is decidedly short [1·337(13) Å], suggesting a bond order of *ca.* 1·3.[10] It adjoins the Pd–O(1) bond which, at 2·008(6) Å, is close to the value found in other comparable compounds. This bond lies *trans* to the isocyanide ligand. Structures which are directly comparable include $(CNBu^t)_2Ni\cdot C(CF_3)_2NH\cdot C(CF_3)_2O$,[11] $(Ph_3P)_2Pt\cdot OCMe_2O_2$,[12] $Pd\cdot(OC_9H_6N)_2$,[13] $(Ph_3P)_2PtOC(Ph)NN(CPhO)$,[14] $Mn[\cdot OC(O)\cdot NH\cdot NH_2]_2$,[15] and $(Ph_3P)_2Pt\cdot OC(CF_3)_2O\cdot C(CF_3)_2O$,[16] in which similarly short bonds were found between an oxygen atom attached to a metal and the adjacent carbon atom (lengths range from 1·31(2) to 1·35(2) Å). These values are similar to those of C(*sp*²)–O bonds in phenols, carboxylic acid derivatives,[17] and thiocarbamates such as $Pd[S\cdot C(OEt)N(R)]_2$ [18,19] where the shortening is usually attributed to electron delocalisation *via* adjacent

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π-bonded systems. In the present compound, C(2) is uniquely placed in that it is surrounded by four highly electronegative groups which will tend to lower the energies of the antibonding orbitals for both the C–CF$_3$ and C–F bonds,[20] while O(1) is likely to have the energies of its lone-pair orbitals raised as a result of its proximity to the electropositive metal atom. Electron delocalisation from O(1) towards C(2), with increase of the C(2)–O(1) bond order, is therefore possible. Standard deviations on the $>$C(CF$_3$)$_2$ parameters do not allow accurate assessment of small changes in bond length corresponding to occupation of antibonding orbitals.

The five-membered ring is not accurately planar, but has an envelope conformation; the atom O(1) deviates from the plane of C(2), O(2), C(1), Pd by some 0·20 Å (see Figure 1 and Table 3). The four CF$_3$ groups have mean C–CF$_3$ 1·512(25) Å, and the angle between the two C–C bonds for the two groups on the same carbon atom does not differ significantly from the ideal tetrahedral value. Also, the plane defined by these two C–C bonds is perpendicular to that defined by the two adjoining ring bonds. The mean C–F bond length is 1·325(19) Å, compared with a mean for many fluorocarbons of 1·333(5) Å.[17] The fluorine atoms have high thermal activity, but a difference synthesis made without any contribution from the fluorine atoms showed no evidence for structural disorder. The bond lengths given in Table 2 have not been corrected for the effects of thermal motion.

CNBu^t *Ligand*.—The Pd–C distance [1·891(9) Å] is notably shorter than that expected for a single bond (*ca.* 2·00 Å) but is similar to distances found in other isocyanide complexes.[21–25] Some degree of multiple bonding in the Pd–C distance can certainly be inferred, but the C–N distance [1·149(11) Å] is not significantly different from that found in a variety of isocyanide molecules (mean 1·16 Å).[17,21–26] The N(3)–C(30) distance [1·482(13) Å] is as expected, as are the three C–Me bonds [mean 1·521(35) Å]. The Pd–C(3)–N(3)–C(30) sequence is approximately, but not accurately, linear.

{C(NEt$_2$NHBu^t} (*Carbene*) *Ligand*.—Here the metal–carbon distance [2·074(9) Å] is at least that expected for a bond between Pd and C(sp^2), suggesting an almost total absence of π-bonding in this link. It is to be expected, therefore, that the other two bonds of the carbenoid link will be correspondingly shorter, and this is borne out by their determined distances [C–NEt$_2$ 1·337(12), C–N(H)Bu^t, 1·294(12) Å]; both may be compared with an expected C(sp^2)–N(sp^2) length of *ca.* 1·44 Å,[9,27] and with distances [1·309(6)—1·362(6) Å] found in other carbenes.[2,28] As a result of the bonding delocalisation in the N–C–N fragment, the atoms Pd, C(4), N(5), C(51), C(61), N(4), H(400), and C(40) are all substantially coplanar (see Table 3). The C–C bonds of the Et and Bu^t groups are all as expected (within 3σ).

The most unusual feature of the carbene ligand, however, is the very short intramolecular contact between H(400) [attached to N(4)] and H(611) on the methylene carbon atom of the 'inner' ethyl group. This was predicted from the n.m.r. spectrum [1] and is confirmed crystallographically from the intramolecular distance of only 1·78 Å between the calculated positions of these two atoms (assuming no angular deformation). Other nearby atoms also show short contact distances with H(400) [namely: N(5) 2·34, C(61) 2·24, C(43) 2·40, and C(62) 2·65], and with H(611) [N(4) 2·50, and C(4) 2·67 Å].

Co-ordination Around Palladium.—Because of the formation of a five-membered ring, an accurately square-planar configuration is not possible. The angle within the ring is 81·7(3)°, and the opposite angle is symmetrically placed [86·3(4)°]. The bonds around Pd are tetrahedrally distorted, the four atoms being alternately 0·03 Å above and below the mean plane (Table 3).

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