Crystal and Molecular Structures of Two Addition Products of Hexafluorobut-2-yne with Palladium(II) β-Diketonate Rings: *cis*-bis[1,2-bis(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl-*O,C*^{1}]palladium(II) and *ab*-[1,2-Bis(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl-*O,C*^{1}]-*cd*-{2-[(dimethylamino)methyl]phenyl-*C*^{1},*N*}palladium(II)

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The crystal structures of the title compounds $C_{18}H_{14}F_{12}O_2Pd$ (1) and $C_{18}H_{19}F_6NO_2Pd$ (2) have been determined. Crystals of (1) are monoclinic, space group $P2_1/n$ with $a = 9.512 \pm 0.007$, $b = 23.294 \pm 0.013$, $c = 11.301 \pm 0.009$ Å, $\beta = 114.9 \pm 0.2°$; crystals of (2) are monoclinic, space group $P2_1/c$, with $a = 8.789 \pm 0.007$, $b = 13.186 \pm 0.010$, $c = 17.237 \pm 0.014$ Å, $\beta = 102.4 \pm 0.2°$. The structures were solved from counter intensity data by heavy-atom techniques and refined by block-diagonal least-squares methods to R 0.057 [4 302 reflections, (1)] and 0.034 [3 748 reflections, (2)]. The molecular geometries are described and related to the fact that both adducts are formed by 1,4-addition of hexafluorobut-2-yne to palladium(II)–acetylacetonate rings. Mean bond lengths are Pd–C 1.998, Pd–O 2.130, Pd–N 2.115, Pd–C(Ph) 1.988, and C=C 1.339 Å.

THE 1,4-addition of hexafluorobut-2-yne (C_4F_6) across certain d^8 rhodium(I)–β-diketonate rings has recently been reported [1] and one of the products so obtained has been the subject of a single-crystal *X*-ray structure determination.[2] As reported in a preliminary communication [3] this 1,4-addition reaction may be extended to d^8

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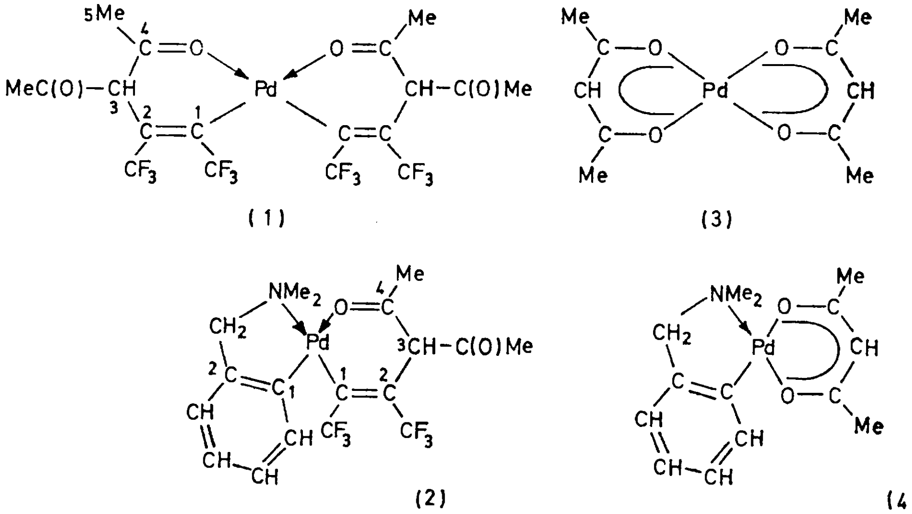
[1] D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt, and B. Y. Kimura, *J.C.S. Dalton*, 1972, 2549.

[2] D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1971, 331.

[3] A. C. Jarvis, R. D. W. Kemmitt, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *J. Organometallic Chem.*, 1974, **66**, C53.

palladium(II)–β-diketonate rings. In confirmation of this we report here the crystal and molecular structures of the adducts (1) and (2) obtained on treating C_4F_6 with bis(acetylacetonato)palladium(II) (3) and (acetylacetonato){2-[(dimethylamino)methyl]phenyl-C^1,N}palladium(II) (4).[4]



(1) (3)

(2) (4)

Showing the systematic numbering

EXPERIMENTAL

Crystal Data.—$C_{18}H_{14}F_{12}O_4Pd$, (1), $M = 628.7$, Monoclinic, $a = 9.512 \pm 0.007$, $b = 23.294 \pm 0.013$, $c = 11.301 \pm 0.009$ Å, $\beta = 114.9 \pm 0.2°$, $U = 2271.2$ Å^3, $D_c = 1.84$ g cm^{-3}, $F(000) = 1\,232$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 9.24 cm^{-1}. Space group $P2_1/n$ from systematic absences: $h0l$ for $h + l = 2n + 1$, $0k0$ for $k = 2n + 1$.

$C_{18}H_{19}F_6NO_2Pd$ (2), $M = 501.8$, Monoclinic, $a = 8.789 \pm 0.007$, $b = 13.186 \pm 0.010$, $c = 17.237 \pm 0.014$ Å, $\beta = 102.4 \pm 0.2°$, $U = 1\,951.4$ Å^3, $D_c = 1.71$ g cm^{-3}, $F(000) = 1\,000$. μ(Mo-K_α) = 10.10 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$.

Crystals of (1) from benzene–light petroleum are plates on {101} with forms {010}, {$11\bar{1}$}, and {$\bar{1}11$} commonly developed. Crystals of (2) from dichloroethane–light petroleum are parallelipipeds with forms {$10\bar{1}$}, {011}, and {$0\bar{1}1$} developed. Unit-cell dimensions were obtained from precession photographs by use of Mo-K_α radiation.

The intensities of reflections with 0.1 Å^{-1} > sinθ/λ < 0.7 Å^{-1} were measured on a Stoe Weissenberg diffractometer by use of monochromatic Mo-K_α radiation and a ω-scan technique. Corrections for Lorentz, polarisation, and absorption[5] effects were made. Intensity data for (1) were collected in 13 layers from a crystal of dimensions *ca.* 0.03 × 0.03 × 0.05 cm mounted about [$10\bar{1}$]. 4 302 Unique reflections having $I > 3\sigma(I)$ were considered observed. Intensity data for (2) were collected in 17 layers from a crystal of dimensions *ca.* 0.02 × 0.03 × 0.04 cm mounted about [001]. 3 748 Unique reflections were considered observed.

Structure Determinations.—Scattering factors were taken from ref. 6. During the least-squares refinement corrections were made for anomalous dispersion.[7] Both structures were solved by conventional heavy-atom techniques and refined by a block-diagonal least-squares treatment. In both cases hydrogen atoms were located from difference-Fourier syntheses calculated after several cycles of refinement and were subsequently included in the structure-factor calculations with a temperature factor of B 5.0 Å^2. Anisotropic temperature factors for all non-hydrogen atoms were refined but hydrogen-atom parameters were not. Weighting schemes were introduced in order that $w\Delta^2$ be approximately independent of $|F_o|$. For (1) twelve cycles of refinement reduced R to 0.057 [$R' = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o| = 0.069$, where $w = (10.0 + |F_o| + 0.02|F_o|^2)^{-1}$] on 4 302 reflections. The maximum shift in the final cycle was 0.8σ. For (2), seven cycles of refinement reduced R to 0.034 [R' 0.042 where $w = (2.8 + 0.067|F_o| + 0.0055|F_o|^2)^{-1}$] on 3 748 reflections. The maximum shift in the final cycle was 0.7σ.

Difference-Fourier syntheses calculated from the final parameters show no maxima >0.3 for (1) or 0.2 eA^{-3} for (2).

RESULTS AND DISCUSSION

Atomic co-ordinates* for (1) and (2) are listed in Tables 1 and 2, and bond lengths and angles in Tables 3 and 4. The large and highly anisotropic temperature factors of the fluorine atoms in (1) are probably caused by libration of the trifluoromethyl groups about the C–CF_3 bonds. By referring the fluorine-atom temperature factors to the local axial system defined in Figure 1 it is evident that the largest root-mean-square amplitude of vibration is perpendicular to the C–F bond and tangential to the circle drawn through the three fluorine atoms. Table 3 also lists corrected C–F bond lengths. The quantity

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* Anisotropic temperature factors have been deposited with the structure factors.

[4] A. C. Jarvis and R. D. W. Kemmitt, 1974, unpublished results.

[5] J. De Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014; N. W. Alcock, *ibid.*, 1969, **A25**, 518.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

$U_z^{F_i} - U_z^{C_a} \cdot (U_x^{F_i}/U_x^{C_a} + U_y^{F_i}/U_y^{C_a})/2$, where U_j^A is the mean square amplitude of vibration of atom A in the direction j of the local axial system (defined in Figure 1), is assumed to be due solely to libration about the C_b–C_aF_3 bond. The value of r (Figure 1) was corrected[8] for libration and the corrected C_a–F_i bond length computed. The fluorine atom temperature factors in (2) are not markedly anisotropic and no libration correction

TABLE 1

Atomic co-ordinates for (1) with standard deviations, in parentheses, derived from the least-squares treatment

	x/a	y/b	z/c
Pd	0.22025(5)	0.16938(2)	0.01147(4)
C(1)	0.3031(7)	0.0997(2)	0.1226(6)
C(2)	0.3017(7)	0.0989(2)	0.2401(6)
C(3)	0.2224(7)	0.1466(2)	0.2820(5)
C(4)	0.2881(6)	0.2051(2)	0.2770(5)
C(5)	0.3820(11)	0.0569(3)	0.3494(8)
C(6)	0.3911(10)	0.0555(3)	0.0814(8)
C(7)	0.0446(7)	0.1498(3)	0.2049(6)
C(8)	−0.0407(10)	0.0941(3)	0.1932(10)
C(9)	0.3212(8)	0.2450(3)	0.3886(6)
C(11)	0.1082(7)	0.1299(3)	−0.1583(6)
C(12)	0.1252(8)	0.1510(3)	−0.2633(6)
C(13)	0.2296(8)	0.2026(3)	−0.2507(6)
C(14)	0.1865(6)	0.2532(3)	−0.1897(6)
C(15)	0.0393(12)	0.1297(4)	−0.4029(7)
C(16)	−0.0087(11)	0.0863(3)	−0.1683(8)
C(17)	0.4032(8)	0.1889(4)	−0.1749(7)
C(18)	0.4688(12)	0.1439(6)	−0.2321(11)
C(19)	0.1751(8)	0.3101(3)	−0.2499(7)
O(1)	0.3145(4)	0.2200(2)	0.1835(4)
O(2)	−0.0174(5)	0.1951(2)	0.1654(5)
O(11)	0.1625(4)	0.2477(2)	−0.0910(4)
O(12)	0.4803(6)	0.2148(3)	−0.0785(6)
F(1)	0.5388(6)	0.0529(3)	0.1624(6)
F(2)	0.3368(8)	0.0031(2)	0.0719(7)
F(3)	0.3881(11)	0.0660(3)	−0.0329(6)
F(4)	0.4993(9)	0.0806(3)	0.4413(7)
F(5)	0.4244(12)	0.0091(3)	0.3193(7)
F(6)	0.2916(8)	0.0411(3)	0.4070(6)
F(11)	−0.0302(17)	0.0805(7)	−0.0735(8)
F(12)	−0.1411(9)	0.0931(5)	−0.2523(10)
F(13)	0.0179(13)	0.0393(3)	−0.1816(22)
F(14)	−0.1024(10)	0.1398(6)	−0.4553(7)
F(15)	0.0442(16)	0.0758(4)	−0.4138(7)
F(16)	0.0979(13)	0.1467(5)	−0.4775(7)
H(81)	−0.140	0.094	0.111
H(82)	0.022	0.059	0.193
H(83)	−0.072	0.089	0.269
H(91)	0.256	0.280	0.357
H(92)	0.286	0.225	0.453
H(93)	0.430	0.254	0.432
H(3)	0.245	0.139	0.375
H(181)	0.434	0.103	−0.218
H(182)	0.415	0.147	−0.335
H(183)	0.579	0.144	−0.205
H(191)	0.124	0.339	−0.215
H(192)	0.280	0.325	−0.236
H(193)	0.111	0.307	−0.347
H(13)	0.210	0.214	−0.341

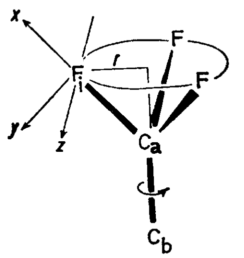

FIGURE 1 Local axial system used in calculating the libration correction for a trifluoromethyl fluorine atom

TABLE 2

Atomic co-ordinates for (2), with standard deviations in parentheses

	x/a	y/b	z/c
Pd	0.35203(3)	0.30606(2)	0.42503(1)
C(1)	0.0758(5)	0.1778(3)	0.4164(3)
C(2)	−0.0664(6)	0.1318(5)	0.4356(4)
C(3)	0.1342(5)	0.1402(3)	0.3441(3)
C(4)	0.1417(4)	0.2280(3)	0.2877(2)
C(5)	0.2289(4)	0.3086(2)	0.3125(2)
C(6)	0.0336(5)	0.2088(3)	0.2086(3)
C(7)	0.2220(4)	0.4023(3)	0.2628(2)
C(8)	0.2865(5)	0.0801(3)	0.3755(3)
C(9)	0.4032(6)	0.0727(4)	0.3239(4)
C(10)	0.5559(4)	0.3481(2)	0.4031(2)
C(11)	0.6063(5)	0.3461(3)	0.3321(3)
C(12)	0.7581(5)	0.3747(4)	0.3292(3)
C(13)	0.8606(5)	0.4050(4)	0.3962(4)
C(14)	0.8160(5)	0.4050(3)	0.4679(3)
C(15)	0.6632(4)	0.3775(3)	0.4724(2)
C(16)	0.6086(5)	0.3795(3)	0.5470(3)
C(17)	0.5507(6)	0.2001(3)	0.5611(3)
C(18)	0.3887(7)	0.3276(5)	0.6033(3)
N(1)	0.4815(4)	0.3030(2)	0.5435(2)
O(1)	0.1440(3)	0.2467(2)	0.4567(2)
O(2)	0.2986(5)	0.0363(3)	0.4370(3)
F(1)	−0.1145(3)	0.1997(3)	0.2181(2)
F(2)	0.0323(5)	0.2767(3)	0.1537(2)
F(3)	0.0638(4)	0.1211(2)	0.1776(2)
F(4)	0.0760(3)	0.4380(2)	0.2390(2)
F(5)	0.2784(3)	0.3918(2)	0.1967(2)
F(6)	0.3028(4)	0.4798(2)	0.3013(2)
H(3)	0.047	0.094	0.315
H(11)	0.530	0.325	0.282
H(12)	0.767	0.375	0.279
H(13)	0.966	0.428	0.396
H(14)	0.891	0.429	0.517
H(21)	−0.136	0.186	0.457
H(22)	−0.133	0.098	0.391
H(23)	−0.039	0.081	0.482
H(91)	0.375	0.028	0.277
H(92)	0.421	0.144	0.306
H(93)	0.503	0.048	0.359
H(161)	0.570	0.450	0.557
H(162)	0.699	0.364	0.595
H(171)	0.475	0.148	0.535
H(172)	0.650	0.196	0.544
H(173)	0.570	0.189	0.621
H(181)	0.274	0.318	0.580
H(182)	0.413	0.270	0.648
H(183)	0.412	0.391	0.629

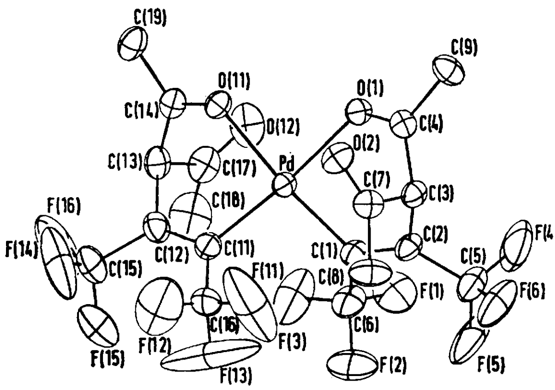

FIGURE 2 Molecular geometry, and atom numbering used in the crystal-structure determination of (1); thermal ellipsoids scaled to 30% probability

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[8] H. Lipson and W. Cochran, 'The Crystalline State,' vol. III, Bell, London, 1966, p. 354.

TABLE 3

Bond lengths (Å) and angles (°) for (1), with estimated standard deviations of bond lengths in parentheses. For angles, no estimated standard deviation is >0.8°. The molecule comprises two similar halves and, where appropriate, equivalent values for each half are separated by a comma [*e.g.* the entry labelled C(1)–C(2) gives the C(1)–C(2) bond length followed by the C(11)–C(12) bond length]. C–F Bond lengths corrected for libration are given in square brackets after the uncorrected length

Pd–C(1)	2.001(5), 1.985(6)
Pd–O(1)	2.106(4), 2.122(4)
C(1)–C(2)	1.333(8), 1.356(8)
C(2)–C(3)	1.525(8), 1.527(10)
C(3)–C(4)	1.510(8), 1.507(9)
C(4)–O(1)	1.233(6), 1.236(7)
C(1)–C(6)	1.519(8), 1.475(10)
C(2)–C(5)	1.507(9), 1.522(10)
C(4)–C(9)	1.491(8), 1.473(9)
C(3)–C(7)	1.544(8), 1.539(10)
C(7)–C(8)	1.506(9), 1.499(12)
C(7)–O(2)	1.200(8), 1.190(10)
C(6)–F(1)	1.32(1), 1.18(1) [1.34, 1.39]
C(6)–F(2)	1.31(1), 1.23(1) [1.33, 1.32]
C(6)–F(3)	1.30(1), 1.15(1) [1.38, 1.36]
C(5)–F(4)	1.29(1), 1.25(1) [1.37, 1.33]
C(5)–F(5)	1.28(1), 1.26(1) [1.36, 1.35]
C(5)–F(6)	1.33(1), 1.25(1) [1.36, 1.37]
C(1)–Pd–C(11)	98.1
O(1)–Pd–O(11)	86.2
C(1)–Pd–O(1)	88.4, 87.7
Pd–C(1)–C(2)	118.0, 117.7
C(1)–C(2)–C(3)	120.9, 121.1
C(2)–C(3)–C(4)	112.2, 111.5
C(3)–C(4)–O(1)	121.5, 121.4
C(4)–O(1)–Pd	117.9, 118.8
Pd–C(1)–C(6)	118.7, 118.3
C(2)–C(1)–C(6)	122.3, 123.1
C(1)–C(2)–C(5)	127.6, 125.4
C(3)–C(2)–C(5)	111.4, 113.4
C(2)–C(3)–C(7)	115.3, 113.1
C(4)–C(3)–C(9)	107.9, 110.0
C(3)–C(4)–C(9)	118.3, 118.3
C(1)–C(4)–C(9)	120.2, 120.3
O(3)–C(7)–C(8)	115.4, 116.7
C(3)–C(7)–O(2)	120.2, 120.5
O(2)–C(7)–C(8)	124.2, 122.8

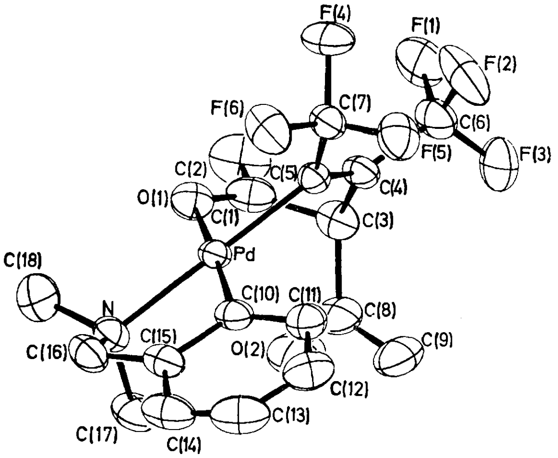

FIGURE 3 Molecular geometry, and atom numbering used in the crystal-structure determination of (2); thermal ellipsoids scaled to 40% probability

was made. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21328 (43 pp., 1 microfiche).* The molecular geometry and atom numbering is shown for (1) in Figure 2 and for (2) in Figure 3.

Both adducts are formed by a 1,4-addition of C_4F_6 to the palladium(II)–acetylacetonate ring(s) in their respective precursors.[4] The acetylene links the γ-carbon of the ring to the metal. Whereas similar additions to rhodium(I) [1] and iridium(I)[9] β-diketonate rings lead to an increase in co-ordination number of the metal, these palladium(II) systems remain four-co-ordinate and one of the carbonyl functions of the original diketonate is not co-ordinated in the adduct. The co-ordination of palladium is essentially planar in both complexes (Table 5), with small tetrahedral distortions; however the palladium atom in (2) does not lie in the mean plane of the four atoms co-ordinated to it.

TABLE 4

Bond lengths (Å) and angles (°) in (2), with estimated standard deviations of bond lengths in parentheses. For angles no estimated standard deviation is >0.5°

Pd–C(5)	2.009(3)	O(1)–Pd–N(1)	93.4
Pd–O(1)	2.163(3)	C(5)–Pd–C(10)	97.6
C(5)–C(4)	1.327(5)	O(1)–Pd–C(5)	86.6
C(4)–C(3)	1.522(5)	N(1)–Pd–C(10)	82.4
C(3)–C(1)	1.528(7)		
C(1)–O(1)	1.220(5)	Pd–O(1)–C(1)	117.7
C(5)–C(7)	1.497(5)	O(1)–C(1)–C(3)	119.7
C(4)–C(6)	1.507(5)	C(1)–C(3)–C(4)	110.0
C(1)–C(2)	1.488(6)	C(3)–C(4)–C(5)	120.3
C(3)–C(8)	1.550(6)	C(4)–C(5)–Pd	116.9
C(8)–C(9)	1.497(8)	C(2)–C(1)–O(1)	120.7
C(8)–O(2)	1.192(6)	C(2)–C(1)–C(3)	119.6
C(6)–F(1)	1.351(6)	C(1)–C(3)–C(8)	107.3
C(6)–F(2)	1.301(6)	C(4)–C(3)–C(8)	117.4
C(6)–F(3)	1.325(6)	C(3)–C(8)–C(9)	118.4
C(7)–F(4)	1.346(4)	C(3)–C(8)–O(2)	117.4
C(7)–C(5)	1.343(5)	C(9)–C(8)–O(2)	123.6
C(7)–F(6)	1.337(4)	C(3)–C(4)–C(6)	110.2
Pd–C(10)	1.988(4)	C(5)–C(4)–C(6)	129.4
Pd–N(1)	2.115(3)	C(9)–C(5)–C(7)	121.8
C(10)–C(11)	1.388(6)	Pd–C(5)–C(7)	120.9
C(11)–C(12)	1.398(6)		
C(12)–C(13)	1.364(6)	C(10)–C(11)–C(12)	120.8
C(13)–C(14)	1.374(6)	C(11)–C(12)–C(13)	120.8
C(14)–C(15)	1.409(6)	C(12)–C(13)–C(14)	119.8
C(15)–C(10)	1.408(5)	C(13)–C(14)–C(15)	120.5
C(15)–C(16)	1.465(7)	C(14)–C(15)–C(10)	119.9
		C(15)–C(10)–C(11)	118.1
C(16)–N(1)	1.497(5)	Pd–C(10)–C(11)	129.3
N(1)–C(17)	1.491(5)	Pd–C(10)–C(15)	112.5
N(1)–C(18)	1.480(7)	C(10)–C(15)–C(16)	117.6
		C(15)–C(16)–N(1)	109.5
		C(16)–N(1)–Pd	105.6
		C(19)–C(15)–C(16)	122.5
		C(17)–N(1)–C(18)	108.6
		C(17)–N(1)–Pd	109.2
		C(17)–N(1)–C(16)	109.7
		C(16)–N(1)–C(18)	110.0
		C(18)–N(1)–Pd	113.9

With the exception of the Pd–O bonds, equivalent

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[9] A. C. Jarvis, R. D. W. Kemmitt, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *J.C.S. Chem. Comm.*, 1974, 797.

TABLE 5

Parameters of mean planes through sets of atoms and (in square brackets) distances (Å) of atoms from the planes. The equation of a plane is $lx + my + nz = p$, with co-ordinates (Å) referred to orthogonal axes a', b, and c

	l	m	n	p
(*a*) Compound (1)				
Plane (i)				
Pd, C(1), C(11), O(1), O(11)	0.9936	0.0239	−0.1104	2.112
[Pd 0.00, C(1) 0.09, C(11) −0.09, O(1) −0.09, O(11) 0.09]				
Plane (ii)				
Pd, C(1), C(2), C(6)	0.7534	0.4847	0.4443	3.484
[Pd 0.02, C(1) −0.07, C(2) 0.03, C(6) 0.02]				
Plane (iii)				
C(1)—(3), C(5)	0.7619	0.5497	0.3426	3.450
[C(1) 0.01, C(2) −0.02, C(3) 0.01, C(5) 0.01]				
Plane (iv)				
Pd, C(11), C(12), C(16)	0.7066	−0.6766	0.2071	−1.187
[Pd 0.02, C(11) −0.06, C(12) 0.02, C(16) 0.02]				
Plane (v)				
C(11)—(13), C(15)	0.7615	−0.6294	0.1551	−0.791
[C(11) 0.01, C(12) −0.02, C(13) 0.01, C(15) 0.01]				
Plane (vi)				
O(1), C(3), C(4), C(9)	0.8107	−0.3695	0.4541	0.678
[O(1) 0.00, C(3) 0.00, C(4) 0.00, C(9) 0.00, Pd −0.43]				
Plane (vii)				
Pd, O(1), C(4)	0.7524	−0.5625	0.3428	−0.643
Plane (viii)				
O(11), C(13), C(14), C(19)	0.7997	0.1649	0.5774	1.994
[O(11) 0.00, C(13) 0.00, C(14) 0.00, C(19) 0.00, Pd 0.36]				
Plane (ix)				
Pd, O(11), C(14)	0.7502	0.3488	0.5617	2.973
Dihedral angles (°)				
(ii)–(iii)	6.9	(iii)–(iv)	5.1	
(vi)–(vii)	13.2	(viii)–(ix)	11.0	
(*b*) Compound (2)				
Plane (i)				
Pd, N(1), O(1), C(5), C(10)	0.3027	−0.9448	−0.1250	−4.210
[Pd −0.03, N(1) −0.03, O(1) 0.05, C(5) −0.03, C(10) 0.05]				
Plane (ii)				
C(10)—(15)	0.2692	−0.9488	0.1653	−2.308
[C(10) −0.01, C(11) 0.01, C(12) 0.00, C(13) −0.01, C(14) 0.01, C(15) 0.00, C(16) −0.02, N(1) 0.63, Pd 0.07]				
Plane (iii)				
Pd, C(4), C(5), C(7)	0.8680	−0.3626	−0.3392	−2.561
[Pd −0.01, C(4) −0.02, C(5) 0.04, C(7) −0.02]				
Plane (iv)				
C(3)—(6)	0.8431	−0.4365	−0.3142	−2.702
[C(3) −0.01, C(4) 0.02, C(5) −0.01, C(6) −0.01]				
Plane (v)				
C(1)—(3), O(1)	0.4598	−0.6734	0.5788	2.067
[C(1) 0.01, C(2) 0.00, C(3) 0.00, O(1) 0.00, Pd 0.06]				
Plane (vi)				
Pd, O(1), C(1)	0.3970	−0.6098	0.6860	2.101
Dihedral angles				
(iii)–(iv)	4.7	(v)–(vi)	8.0	

bond lengths and angles in each of the three Pd–C–C–C–C–O rings are not significantly different, and the mean values are shown in Figure 4. Those bond lengths and angles not involving the metal are similar to values found when C_4F_6 adds across rhodium(I)[1] and iridium(I)[9] acetylacetonato-rings.

The mean Pd–O bond in (1) is significantly shorter than that in (2) because the *trans*-carbon atoms in the former have strongly electron-withdrawing CF_3 groups as substituents. The longer Pd–O bond length of (2) is similar to that (2.158 Å) reported for [Pd(acac)($C_{18}H_{20}$)].[10] There are two distinct C=O bond lengths with the co-ordinated ketonic bond being the longer, as expected. Both C=O bonds are shorter than the mean value observed in (3)[11] (1.31_5 Å), indicative of the greater carbon–oxygen bond orders in (1) and (2). The value of the mean C=C bond length compares well with that (1.336 Å) in ethylene.[12] The C(sp^3)–C(sp^2) bond lengths are unexceptional except for the >CH–C(O)Me bond which is consistently longer than expected [*cf.* C(sp^2)–C(sp^3) 1.510 Å (ref. 13)]. The Pd–C–C–C–C–O rings show further deviations from ideal geometry. The C(CF_3)=C–CF_3 angle is significantly larger than 120°, presumably in order to minimise steric interference between the adjacent CF_3 groups. Similarly the C(CF_3)–CH–C(O)Me angle is larger than tetrahedral. The carbon atom bonded to palladium is on average 0.08 Å out of the mean plane of its attached atoms. The C(CF_3)=C(CF_3) and co-ordinated C=O bonds have mean torsion angles of 6 and 11° respectively. The mean (corrected) C–F bond length (1.35 Å) is similar to the accepted value of 1.333 Å.[13]

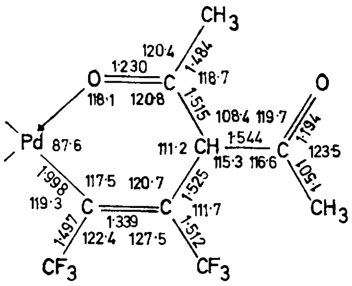

FIGURE 4 Mean bond lengths (Å) and angles (°) of the Pd–C–C–C–C–O rings in (1) and (2)

The phenyl ring in (2) is planar (Table 5), mean C–C bond length 1.390(7) Å and mean C–C–C angle 120.0(5)°. The mean C–N bond length (1.489 Å) compares well with the value (1.479 Å) for a C(sp^3)–N(four-co-ordinate) bond, given in ref. 13. The nitrogen atom is on the same side of the phenyl-ring plane as the non-bonded carbonyl

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[10] C. Calvo, T. Hosokana, H. Reinheimer, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1972, **94**, 3237.

[11] A. N. Knyazeva, E. A. Shugan, and L. M. Shkol'nikova, *Zhur. Strukt. khim.*, 1970, **11**, 938.

[12] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, 1965, **42**, 2683.

[13] *Chem. Soc. Special Publ.*, No. 18, 1965.

function with the methyl groups C(17)H_3 and C(18)H_3 in axial and equatorial positions respectively (Figure 3). The observed conformation of the five-membered Pd–C–C–C–N ring, as opposed to the alternative with nitrogen on the opposite side of the phenyl plane, minimises steric interaction between the phenyl carbon atom C(11) and the fluorine atoms attached to C(7).

The orientation of the non-bonded carbonyl groups is of interest. In (1) the distances Pd–C(7), Pd–C(17), Pd–O(2), and Pd(12) are 3.30, 3.28, 3.23, and 3.43 Å with the C=O bond approximately perpendicular to the line connecting the midpoint of the bond to the metal, (*i.e.* in a 'π-bonding' orientation). Because this orientation of the carbonyl group is not expected on simple steric grounds, and bearing in mind evidence for weakly bonding axial interactions in other square-planar Pd^{II} species {*e.g. trans*-[$PdI_2(PMe_2Ph)_2$] (ref. 14)}, we tentatively suggest a weak π-interaction between the metal and the non-bonded carbonyl function. Whether or not this is the case, the orientation of the non-bonded carbonyl groups suggests the previously reported[3] mechanism whereby the two different methyl environments in (1) may be made equivalent in solution at room temperature (*viz.* a concerted mechanism whereby the two long Pd–O bonds shorten to form an octahedral intermediate which undergoes a trigonal twist, followed by reversal of the initial process to yield an equivalent structure with the methyl groups interchanged). The non-bonded carbonyl group in (2) has a different orientation, namely that expected on steric grounds, with Pd–C(8) 3.12 and Pd–O(2) 3.60 Å. The ^1H n.m.r. spectrum of (2)[4] shows that this molecule is also fluxional in solution at room temperature with both acetylacetonato-methyl groups and both nitrogen-bonded methyl groups equivalent. The two acetylacetonato-methyl groups may be made equivalent by a mechanism similar to that postulated for (1), but producing a five-coordinate intermediate. Minimisation of steric interactions between the CF_3 group adjacent to the metal and the phenyl group would then require a change in conformation of the five-membered Pd–C–C–C–N ring such that the nitrogen atom would move to the other side of

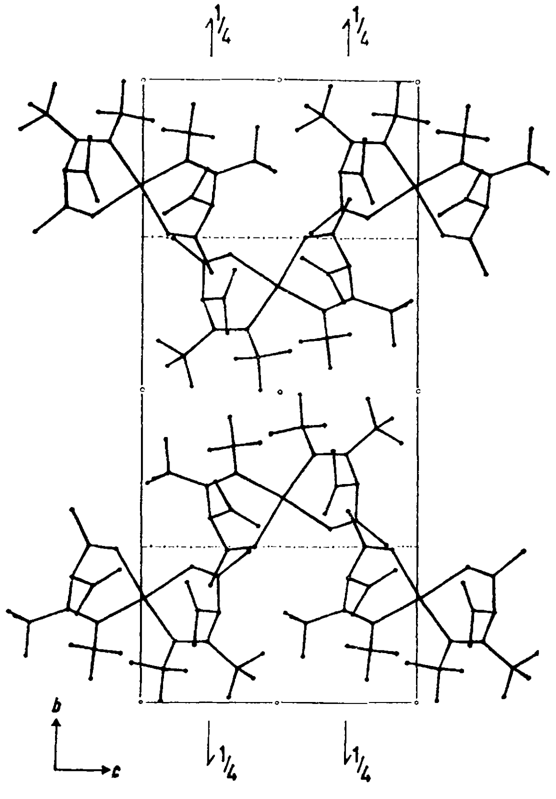

FIGURE 5 Packing of the molecules of (1) in the unit cell, projected along [100]

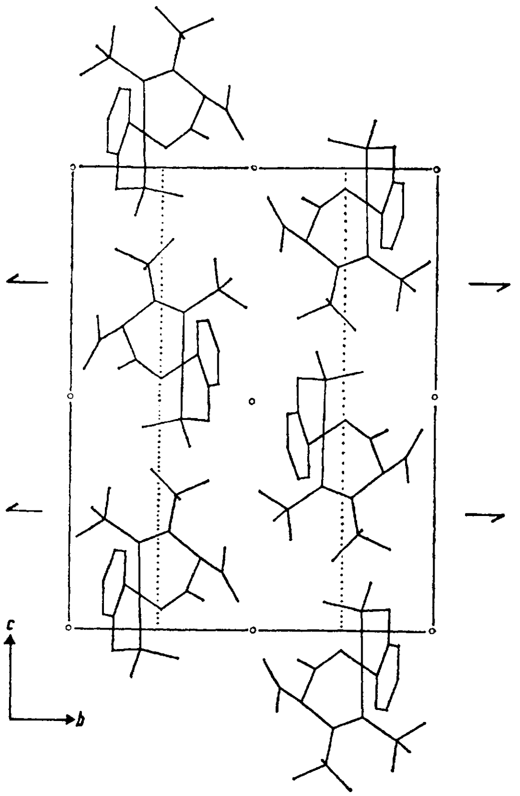

FIGURE 6 Packing of the molecules of (2) in the unit cell, projected along [100]

TABLE 6

Short intermolecular contacts (Å)

Compound (1)		Compound (2)	
C(8) ··· H(192^{I})	2.88	C(12) ··· H(19^{VI})	2.80
O(11) ··· H(93^{II})	2.34	F(4) ··· H(3^{VII})	2.41
O(12) ··· H(193^{III})	2.42	F(1) ··· H(162^{VIII})	2.54
H(82) ··· F(13^{IV})	2.32	H(23) ··· H(23^{IX})	2.30
H(183) ··· H(91^{V})	2.33		

Roman numeral superscripts denote atoms related to those at x, y, z by the symmetry operations

I $x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$
II $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
III $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
IV $-x, -y, -z$
V $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$
VI $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
VII $-x, \frac{1}{2} + y, \frac{1}{2} - z$
VIII $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$
IX $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$

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[14] N. A. Bailey and R. Mason, *J. Chem. Soc.* (*A*), 1968, 2594.

the phenyl-ring plane. This produces an equivalent molecule but with both sets of methyl groups interchanged.

The solid-state packing of the molecules is shown in Figures 5 and 6, both projected along the *a* axis. There are no exceptionally short intermolecular contacts; those few contacts shorter than the estimated sum of van der Waals radii [15] for the atoms are listed in Table 6.

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[4/2171 *Received, 21st October,* 1974]

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[15] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.