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C,O-Chelates of the Trifluoroacetylacetonate Dianion with Palladium(II). Molecular Structure of [Pd(tfac(2−)-*C,O*)(PPh_3)(2,6-Me_2-py)]

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Reactions of bis(trifluoroacetylacetonato)palladium(II), [Pd(tfac)$_2$], with tertiary phosphines followed by pyridine or its derivatives afforded a series of the [Pd(tfac(2−)-*C,O*)LL′]-type complexes which contain a C,O-chelating trifluoroacetylacetonate dianion and a couple of tertiary phosphine and/or heterocyclic nitrogen base ligands (L and L′). Their structures in solution were studied by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy and the molecular structure in a crystal of [Pd(tfac(2−)-*C,O*)(PPh_3)(2,6-Me_2-py)]·C_6H_6 containing triphenylphosphine and 2,6-dimethylpyridine as L and L′ was determined by means of X-ray diffraction.

β-Dicarbonyl compounds are very popular ligands¹⁾ and widely used as chelating monoanions.²⁾ In recent years the reactions of bis(β-diketonato)palladium(II) and -platinum(II) with a variety of nitrogen bases³⁾ and tertiary phosphines³ᵃ,⁴⁾ have been extensively studied to demonstrate transformation of the chelating β-diketonate anion into the central-carbon-bonded⁵⁾ and other bonding states. The η-allylic complexes of monoanions of ethyl acetoacetate⁶⁾ and acetylacetone⁷⁾ were also shown to react with Lewis bases to afford the terminal-carbon-bonded complexes.⁷,⁸⁾

In the course of these studies, four novel coordination modes of β-diketonate dianions have been found: η-allylic coordination of the acetylacetonate dianion to palladium(II)⁹⁾ and platinum(II)¹⁰⁾ and of the dianion of ethyl acetoacetate to palladium(II),⁹⁾ C,O-chelation of the trifluoroacetylacetonate dianion to platinum(II),¹¹⁾ bridging of the acetylacetonate dianion between palladium(II) and another metal *via* the terminal carbon and two oxygen atoms,¹²⁾ and another type of bridging by dianions of acetylacetone and ethyl acetoacetate, η³-bonding to palladium and O,O′-chelating another metal atom.¹³⁾

This paper reports the preparation and NMR characterization of C,O-chelates of the trifluoroacetylacetonate dianion with palladium(II) and also the crystal and molecular structure of one complex containing triphenylphosphine and 2,6-dimethylpyridine as ancillary ligands.

Experimental

Preparation of Complexes. Bis(trifluoroacetylacetonato)-palladium(II), [Pd(tfac)$_2$] (**1**) was prepared by the method reported in a previous paper.¹⁴⁾ Tris(*o*-tolyl)phosphine, P(*o*-tolyl)$_3$, was recrystallized from ethanol. Triphenylphosphine, PPh_3, and nitrogen bases were used as supplied without further purification.

*Trifluoroacetylacetonato(2−)bis(triphenylphosphine)palladium(II)–Diethyl Ether (1/1), [Pd(tfac(2−)-*C,O*)(PPh_3)$_2$]·Et_2O (2):* A dichloromethane solution (0.5 cm³) of 1,8-bis(dimethylamino)naphthalene (21 mg, 0.10 mmol) was added to a solution of **1** (41 mg, 0.099 mmol) and triphenylphosphine (52 mg, 0.20 mmol) in the same solvent and the mixture was left to stand at room temperature for one day. Diethyl ether (8 cm³) and hexane (8 cm³) were added to the solution and the mixture was kept in a refrigerator overnight to deposit yellow needles, which were filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 58 mg (68%). Inclusion of one molecule of diethyl ether per palladium was confirmed by ^{1}H NMR spectroscopy.

*[Pd(tfac(2−)-*C,O*)(PPh_3)(py)] (3):* Pyridine (0.5 cm³, 6 mmol) was added to a dichloromethane solution (5 cm³) containing **1** (75 mg, 0.18 mmol) and triphenylphosphine (96 mg, 0.37 mmol) and the mixture was kept to stand at room temperature for one day. The solution was concentrated to 2 cm³ by evaporation under reduced pressure and diethyl ether was added to the concentrate. Yellow plates deposited after standing for one day at room temperature were filtered, washed with diethyl ether, and dried *in vacuo*. On being washed with diethyl ether, yellow plates lost the solvent of crystallization (dichloromethane), turning opaque. The yield was 60 mg (56%).

*[Pd(tfac(2−)-*C,O*)(PPh_3)(4-Me_2N-py)]·1/2CH_2Cl_2 (4):* 4-(Dimethylamino)pyridine (31 mg, 0.25 mmol) was added to a solution of **1** (103 mg, 0.250 mmol) and triphenylphosphine (131 mg, 0.499 mmol) in benzene (5 cm³) and the mixture was left to stand at room temperature overnight to precipitate yellow needles, which were filtered, washed with a mixture (1:2 by volume) of dichloromethane and hexane, and dried *in vacuo*. The yield was 91 mg (57%). Recrystallization from dichloromethane–hexane gave yellow needles which contain a half molecule of dichloromethane per palladium.

*[Pd(tfac(2−)-*C,O*)(PPh_3)(2,6-Me_2-py)] (5):* 2,6-Dimethylpyridine (3 cm³, 26 mmol) was added to a solution of **1** (805 mg, 1.95 mmol) and triphenylphosphine (1045 mg, 3.98 mmol) in dichloromethane (25 cm³) and the mixture was stirred for 3 h. The solution was concentrated to 5 cm³ by evaporation under reduced pressure and diethyl ether was added to the concentrate to precipitate yellow crystals (1142 mg) in a 91% yield, which were recrystallized from dichloromethane–hexane or benzene. In the former case, yellow plates deposited lost the solvent of crystallization (probably dichloromethane) and turned opaque on being washed with diethyl ether. In the latter case the benzene solvate (**5′**) was obtained, which was submitted for X-ray analysis.

*[Pd(tfac(2−)-*C,O*){P(*o*-tolyl)$_3$}(2,6-Me_2-py)] (6):* 2,6-

Dimethylpyridine (2 cm^3, 17 mmol) was added to a solution of [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}]$^{4b)}$ (215 mg, 0.300 mmol) in dichloromethane (10 cm^3) and the mixture was stirred for 5 h. Addition of diethyl ether to the solution precipitated yellow fuzzy crystals, which were filtered and dried *in vacuo*. The yield was 78 mg (39%).

*[Pd(tfac(2−)-C,O){P(o-tolyl)$_3$}(4-Me$_2$N-py)] (**7**)*: Yellow crystals of **7** were prepared in a manner similar to **6**. The yield was as low as 5% because of formation of [Pd(4-Me$_2$N-py)$_4$](tfac)$_2$ as a by-product.

*[Pd(tfac(2−)-C,O)(2,9-Me$_2$-phen)] (**12**)*: Complex **1** (823 mg, 1.99 mmol) was allowed to react with 2,9-dimethyl-1,10-phenanthroline–water (1/2) (416 mg, 1.91 mmol) in dichloromethane (30 cm^3) at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was dissolved in acetone (5 cm^3). Diethyl ether (10 cm^3) was added to the solution and the mixture was kept in a refrigerator overnight to deposit yellow cubes, which were filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 600 mg (65%).

*[Pd(tfac(2−)-C,O)(4-Me$_2$N-py)$_2$] (**9**)*: Complex **12** (234 mg, 0.501 mmol) and 4-(dimethylamino)pyridine (183 mg, 1.50 mmol) were dissolved in dichloromethane (5 cm^3) and the mixture was left to stand for 1.5 h. On addition of hexane to the solution, yellow needles appeared immediately. After being kept in a refrigerator overnight, the crystals were filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 210 mg (83%).

*[Pd(tfac(2−)-C,O)(py)$_2$] (**8**)*: Yellow needles of **8** were obtained in a 50% yield in the same way as above. This complex dissolves in dichloromethane and acetone but a yellow precipitate deposits promptly, which has not been characterized.

*[Pd(tfac(2−)-C,O)(bpy)] (**10**)*: When a dichloromethane solution (2 cm^3) of 2,2′-bipyridine (156 mg, 1.00 mmol) was added to a solution of **1** (413 mg, 1.00 mmol) in the same solvent (10 cm^3), an orange-red crystalline solid appeared, which was filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 170 mg (41%). Recrystallization was performed from a mixture (1:1 by volume) of chloroform and methanol, the product containing one half molecule of chloroform per palladium. Alternatively, a suspension of [Pd(tfac)(bpy)](tfac)$^{3c)}$ (100 mg, 0.176 mmol) in dichloromethane (5 cm^3) was stirred at 40 °C for 40 min to result in a clear solution, which was cooled spontaneously to room temperature to deposit a yellow precipitate of **10** (27 mg) in a 37% yield.

*[Pd(tfac(2−)-C,O)(phen)] (**11**)*: Compound **11** was obtained in a 30% yield by the reaction of **1** with 1,10-phenanthroline in a manner similar to **10**.

Measurements. IR spectra were recorded in Nujol mull on a Hitachi 295 infrared spectrophotometer. NMR spectra were measured with JEOL FX60Q (for ^{1}H, ^{13}C, and ^{31}P) and FX90Q (for ^{19}F) spectrometers. The molecular weight was determined by vapor pressure osmometry with an instrument manufactured by Knauer in West Berlin, West Germany.

X-Ray Diffraction: Crystal Data. [Pd(tfac(2−)-*C,O*)(PPh$_3$)(2,6-Me$_2$-py)]·(C$_6$H$_6$) (**5′**), $C_{30}H_{24}O_2NF_3PPd\cdot C_6H_6$, F. W. 703.0, monoclinic, $P2_1/c$, $a=10.035(2)$, $b=17.941(6)$, $c=18.903(5)$ Å, $\beta=103.25(2)°$, $V=3312.6(16)$ Å^3, $D_m=1.40$ (flotation), $D_c=1.41$ g cm^{-3} for $Z=4$, μ(Mo $K\alpha$)$=6.51$ cm^{-1}.

The crystal was sealed in a thin-walled glass capillary tube, since it was rather unstable in air. The unit-cell parameters and reflection intensities of **5′** were measured on a Rigaku automated, four-circle diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). Intensity data were collected by the θ-2θ scan technique. The scan rate was 4° min^{-1} and the scan width was $\Delta(2\theta)=(2.0+0.7\tan\theta)°$. The background intensities were measured for 7.5 s at both ends of a scan. Four standard reflections (0, 10, 0, 500, 066, and 555) were measured at regular intervals to monitor crystal stability and orientation, and the intensities of these reflections remained constant throughout the data collection. Usual Lorentz and polarization corrections were made, but no absorption correction was carried out. A total of 6001 (5180 non-zero) reflections was measured ($\sin\theta/\lambda\leqq0.6$).

*Solution and Refinement of the Crystal Structure of **5′**.* The structure was solved by the heavy atom method. Approximate coordinates of the palladium atom were obtained from a three-dimensional Patterson function. Subsequent Fourier synthesis revealed locations of all the non-hydrogen atoms. The existence of the solvated benzene molecule was also discovered. Including the carbon atoms of the crystalline benzene molecule, the structure was refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).$^{15)}$ The function minimized was $\sum w(|F_o|-|F_c|)^2$. Hydrogen atoms except those of terminal methyl groups and solvated benzene molecule were located by the difference Fourier synthesis, and refined isotropically. The final *R* is 0.045 for non-zero (0.063 for all) reflections. The weighting schemes used at the final stage were $w=\{\sigma_{cs}{}^2(F_o)+0.0292|F_o|+0.0010|F_o|^2\}^{-1}$ for $|F_o|>0$ and $w=0.0504$ for $|F_o|=0$; σ_{cs} is the standard deviation obtained by the counting statics. The atomic scattering factors used for non-hydrogen atoms were taken from International Tables for X-Ray Crystallography$^{16)}$ and those for hydrogen atoms from Stewart and co-workers.$^{17)}$ Computations were done on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The final atomic coordinates with equivalent temperature factors$^{18)}$ are given in Table 1.†††

Results and Discussion

Characterization of the Trifluoroacetylacetonate(2−) Complexes. The analytical data for the newly prepared complexes given in Table 2 conform to their proposed formulae, [Pd(tfac(2−)-*C,O*)LL′]. The molecular weight of complex **5** was determined in dichloromethane at 25 °C to be 616 in good agreement with the calculated value 627. In accord with the proposed structure, all complexes show the ν(C=O) bands in 1620—1600-cm^{-1} region, complex **5**, for instance, having a very strong band at 1615 cm^{-1}.

Table 3 presents the ^{1}H NMR spectra in CDCl$_3$. The spectrum of each complex is composed of signals assignable to CH$_2$, CH, L, and L′ protons. The methine proton of tfac dianion resonates in the 5.13—5.28-ppm region, the chemical shift being rather insensitive to natures of the ancillary ligands. On the other hand, the chemical shifts and multiplicities of the methylene signals clearly show dependence on natures of the neutral ligands L and L′, spanning a wider range of 2.54—3.14 ppm. Thus the signal for the methylene protons of **2** appears as a doublet of doublets due to couplings to both the trans and cis phosphorus atoms, ^3J(P–H) being 9.$_5$ and 5.$_9$ Hz,

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††† Tables of anisotropic thermal parameters and observed and calculated structure factors are kept at the Chemical Society of Japan (Document No. 8234).

TABLE 1. FINAL ATOMIC POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Non-hydrogen atoms with equivalent temperature factors.[18]

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Pd	0.30530(3)	0.17523(2)	0.01890(2)	2.78	C(24)	0.4348(6)	0.2900(4)	−0.2423(3)	5.0
P	0.2451(2)	0.28023(6)	−0.04268(6)	2.82	C(25)	0.4167(6)	0.5349(4)	−0.2068(3)	5.0
F(1)	0.5001(5)	−0.0597(2)	0.0982(3)	8.2	C(26)	0.3611(6)	0.3541(3)	−0.1465(3)	4.4
F(2)	0.6287(4)	−0.0193(3)	0.1946(3)	7.7	C(31)	0.2827(5)	0.3676(3)	0.0065(3)	3.6
F(3)	0.4146(4)	−0.0249(2)	0.1838(3)	7.4	C(32)	0.3849(6)	0.3713(3)	0.0704(3)	4.9
N	0.1000(4)	0.1346(2)	0.0134(2)	3.0	C(33)	0.4134(7)	0.4398(4)	0.1054(4)	6.8
O(1)	0.3693(3)	0.0773(2)	0.0749(2)	3.7	C(34)	0.3427(7)	0.5031(4)	0.0778(4)	6.9
O(2)	0.6671(4)	0.2424(2)	0.1292(2)	5.1	C(35)	0.2420(8)	0.4991(3)	0.0161(4)	6.4
C(1)	0.5055(5)	0.2033(3)	0.0244(3)	3.2	C(36)	0.2121(6)	0.4327(3)	−0.0190(3)	4.9
C(2)	0.5930(5)	0.1923(3)	0.0981(3)	3.4	C(41)	0.0310(5)	0.0971(3)	−0.0452(3)	3.9
C(3)	0.5947(4)	0.1190(3)	0.1316(3)	3.5	C(42)	−0.1030(6)	0.0724(4)	−0.0487(4)	5.5
C(4)	0.4903(4)	0.0690(3)	0.1149(3)	3.0	C(43)	−0.1643(5)	0.0863(4)	0.0084(4)	5.8
C(5)	0.5112(5)	−0.0080(3)	0.1480(3)	4.0	C(44)	−0.0902(5)	0.1222(4)	0.0681(4)	5.2
C(11)	0.0610(5)	0.2861(3)	−0.0805(3)	3.8	C(45)	0.0410(5)	0.1464(3)	0.0698(3)	4.0
C(12)	−0.0251(5)	0.2972(3)	−0.0323(4)	4.7	C(46)	0.1027(6)	0.0821(3)	−0.1066(3)	4.9
C(13)	−0.1644(6)	0.2960(4)	−0.0564(5)	6.8	C(47)	0.1238(6)	0.1856(4)	0.1353(3)	5.4
C(14)	−0.2212(7)	0.2823(5)	−0.1269(6)	8.9	C(B1)	0.0575(8)	0.4931(5)	0.1895(4)	8.5
C(15)	−0.1412(7)	0.2739(4)	−0.1775(4)	8.1	C(B2)	−0.0410(9)	0.5241(5)	0.2206(4)	7.8
C(16)	0.0023(6)	0.2746(3)	−0.1547(4)	5.5	C(B3)	−0.1518(8)	0.4809(5)	0.2238(5)	9.2
C(21)	0.3223(5)	0.2874(3)	−0.1210(3)	3.5	C(B4)	−0.1694(8)	0.4084(5)	0.1957(5)	9.0
C(22)	0.3449(6)	0.2222(3)	−0.1557(3)	4.5	C(B5)	−0.0751(9)	0.3794(6)	0.1668(6)	9.8
C(23)	0.4001(7)	0.2231(4)	−0.2169(3)	5.1	C(B6)	0.0420(9)	0.4197(6)	0.1635(5)	9.9

(b) Hydrogen atoms with isotropic temperature factors.

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
H(101)	0.518(4)	0.251(3)	0.009(3)	3(1)	H(25)	0.453(6)	0.391(3)	−0.220(3)	6(2)
H(102)	0.523(5)	0.167(3)	−0.007(3)	4(2)	H(26)	0.343(5)	0.395(3)	−0.123(3)	4(1)
H(301)	0.671(5)	0.107(3)	0.160(3)	4(1)	H(32)	0.435(5)	0.333(3)	0.085(3)	3(1)
H(12)	0.006(6)	0.294(3)	0.020(3)	6(2)	H(33)	0.497(6)	0.431(4)	0.155(4)	8(2)
H(13)	−0.218(6)	0.298(4)	−0.015(4)	7(2)	H(34)	0.343(6)	0.542(4)	0.100(4)	8(2)
H(14)	−0.319(7)	0.280(4)	−0.146(4)	8(2)	H(35)	0.194(5)	0.542(3)	−0.003(3)	5(2)
H(15)	−0.183(5)	0.262(3)	−0.226(3)	6(2)	H(36)	0.149(5)	0.431(3)	−0.062(3)	4(2)
H(16)	0.069(5)	0.266(3)	−0.189(3)	4(2)	H(42)	−0.145(6)	0.045(3)	−0.096(3)	7(2)
H(22)	0.315(6)	0.178(3)	−0.144(3)	5(2)	H(43)	−0.258(6)	0.069(3)	0.009(3)	5(2)
H(23)	0.411(6)	0.172(3)	−0.237(3)	6(2)	H(44)	−0.122(5)	0.132(3)	0.121(3)	6(2)
H(24)	0.472(5)	0.290(3)	−0.283(3)	4(1)					

TABLE 2. ANALYTICAL DATA FOR [Pd(tfac(2−)-*C*,*O*)LL′]

Compd	L	L′	Decomp temp °C	Found(Calcd) (%) C	H	N
2[a]	PPh$_3$	PPh$_3$	90—100	62.58(63.05)	4.83(5.06)	
3	PPh$_3$	py	208—210	55.95(56.06)	3.96(3.86)	2.36(2.34)
4[b]	PPh$_3$	4-Me$_2$N-py	163—166	54.93(54.70)	4.25(4.33)	4.27(4.22)
5	PPh$_3$	2,6-Me$_2$-py	200—203	57.68(57.38)	4.39(4.33)	2.31(2.23)
5′[c]	PPh$_3$	2,6-Me$_2$-py		60.44(61.29)	4.59(4.71)	1.86(1.98)
6	P(o-tolyl)$_3$	2,6-Me$_2$-py	*ca.* 200	59.19(59.16)	5.08(4.96)	2.05(2.09)
7	P(o-tolyl)$_3$	4-Me$_2$N-py	191—195	57.77(57.82)	4.53(4.85)	2.05(2.17)
8	py	py	190—200	43.37(43.24)	3.16(3.14)	6.79(6.72)
9	4-Me$_2$N-py	4-Me$_2$N-py	149—152	44.98(45.39)	4.65(4.61)	10.94(11.14)
10[d]	bpy		200—205	39.62(39.25)	2.51(2.44)	5.85(5.91)
11	phen		*ca.* 210	46.65(46.55)	2.56(2.53)	6.42(6.39)
12	2,9-Me$_2$-phen		*ca.* 150	49.02(48.89)	3.30(3.24)	6.04(6.00)

a) Containing one molecule of diethyl ether per Pd. b) Containing one half molecule of dichloromethane per Pd. c) Containing one molecule of benzene per Pd. d) Containing one half molecule of chloroform per Pd.

Table 3. ^{1}H NMR Data in CDCl$_3$$^{a)}$

Compd	tfac(2−)		L and L′	
	CH$_2$	CH	CH$_3$	Other
2	2.76 dd [9.$_5$, 5.$_9$]	5.13		Ph: 7.3c
3	2.63 d [5.$_4$]	5.32		py: H^{2,6} 8.12 d(5) Ph and H^{3,4,5} of py: 6.9—7.6c
4	2.54 d [5.$_4$]	5.28	2.88	py: H^{3,5} 6.08 d(6.$_6$) Ph and H^{2,6} of py: 7.3c
5	2.70 d [5.$_6$]	5.27	2.81	py: H^{3,5} 6.78 d(6.$_5$) Ph and H^4 of py: 7.35, 7.27c
6	2.68 d [5.$_1$]	5.25	2.83	py: H^{3,5} 6.74 d(7.$_6$) Ph and H^4 of py: 7.3c
9	2.68	5.23	3.04, 2.99	py: H^{2,6} 8.02 d, 7.69 d; H^{3,5} 6.44 d, 6.39 d (each 7)
10$^{b)}$	2.85	5.24		bpy: 7.5—8.5c
12	3.14	5.27	2.17	phen: H^{3,8} 8.26 d; H^{4,7} 7.38 d (each 8.$_4$); H^{5,6} 7.78

a) Chemical shifts in ppm from internal Me$_4$Si. Signals are singlets except those marked with d(doublet), dd(doublet of doublets), and c(complex). Figures in parentheses and brackets give ^3J(CH-CH) and ^3J(P-H) in Hz, respectively. b) In a mixture (1:1 by volume) of CDCl$_3$ and CD$_3$OD at 50 °C.

respectively. The signal pattern closely resembles that of [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$]11) except the ^{195}Pt satellites. The methylene protons of **4**, **5**, and **6** resonate as a doublet with smaller ^3J(P–H) values, indicating that the phosphine ligand lies on the position cis to the methylene in each of these complexes.

In the case of complexes containing the same kind of neutral ligands (L=L′), two sets of signals from L should be observed since the chelating tfac(2−) ligand is unsymmetric. In fact complex **9** shows two kinds of signals assignable to NMe$_2$ and pyridine-CH protons. However, complex **12** exhibits no splitting in signals from ring-CH and Me protons, suggesting some kind of fluxional motion (coordination-site exchange).

The ^{13}C NMR data are listed in Table 4. The methylene carbon of **2** resonates as a doublet owing to coupling to the trans ^{31}P, ^2J(P–C) being 70 Hz. Coupling to the cis ^{31}P is not detected contrary to the case of the corresponding platinum(II) complex in which couplings to both ^{31}P atoms were observed (72 and 4 Hz).11) Complexes **4**, **5**, and **6** exhibit methylene doublets with ^2J(P–C) of 4—5 Hz in accordance with the proposed *cis*(CH$_2$, P) structure. The $\underline{C}F_3\underline{C}O$ carbons of these complexes also couple to ^{31}P, conforming with their positions trans to ^{31}P.

Complexes **2** and **9** exhibit two sets of signals attributable to PPh$_3$ and 4-Me$_2$N-py carbons, reflecting unsymmetry of the tfac(2−) chelate. In the case of **12** at room temperature, the methyl carbons of 2,9-Me$_2$-phen appear as two broad signals, while the ring carbons show one set of rather broad signals. The methyl signals merge at higher temperatures to a broad singlet at 52 °C and signals of the ring carbons are sharpened, indicating equivalence of two halves of the phen molecule. The tfac(2−) carbons are invariably sharp at these temperatures, suggesting that the coordination-site exchange occurs in an intramolecular fashion rapidly on the NMR time scale. Self catalysis by virtue of coordination of a neighboring molecule *via* the carbonyl oxygen of tfac(2−) as was observed for [Pd(acac)(6-chloro-3 or 4-pyridyl)(PPh$_3$)]19) is not a plausible mechanism for the present case, since a free ligand such as pyridine, triphenylphosphine, and tris(*o*-tolyl)phosphine added to a solution of **12** showed no promoting effect. No evidence to support mechanism *via* a three-coordinate20) or a nonplanar four-coordinate21) intermediate as proposed for some complexes has been obtained in the present case. The exact nature of the fluxional motion of **12** is not clear at the present stage of investigation.

The ^{19}F NMR spectrum of **5** shows a broad signal with the half-height width of 2.$_6$ Hz at 72.60 ppm upfield from external CFCl$_3$. The broadness may be caused by coupling to the phosphorus atom situated at the trans position, since the ^{19}F signal from [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$] appears as a doublet owing to coupling to ^{31}P with ^5J(P–F)=1.1 Hz.11) Figure 1 shows the ^{31}P{^{1}H} NMR spectra of **2** and **5** in CDCl$_3$. Complex **5** exhibits a quartet at 37.2$_0$ ppm downfield from external H$_3$PO$_4$ with ^5J(P–F)=0.9 Hz in accord with the proposed trans arrangement. Complex **2** shows an AB quartet (^2J(P–P)=35.$_7$ Hz), reflecting nonequivalence of the two phosphorus atoms. The broad signal at 38.5$_8$ ppm is assigned to P^2 trans to O, since the chemical shift is close to that observed for **5** and the broadening is thought to be caused by coupling to the ^{19}F atoms. The sharp doublet at 22.8$_4$ is thus assigned to P^1 trans to C. It may be worth noting that the relative positions of the P^1 and P^2 signals are reverse of those for [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$].11)

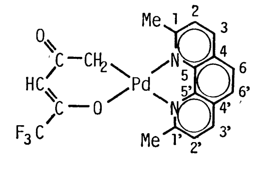
Formation of the Trifluoroacetylacetonato(2−) Complexes. In a previous paper11) [Pt(tfac)$_2$] was reported to react with a Lewis base (L) such as triphenylphosphine, tris(*p*-chlorophenyl)phosphine, and triphenylarsine at room temperature to afford a C,O- chelate of the trifluoroacetylacetonate dianion, [Pt(tfac(2−)-

Table 4. ^{13}C NMR Data in $CDCl_3$[a)]

Compd	tfac(2−)					L and L′
	CH_2	C=O	CH	$CF_3\underline{C}$-O	CF_3	
2	41.0 d [70]	203.7 d [3]	99.6	164.2 q {32}	b)	Ph: C^1 131—133c; C^2 134.1 d [13]; C^3 128.4 d [10], 128.2 d [9]; C^4 130.8 d [3], 129.9 d [3]
3	27.1 d [4]	204.5 d [2]	100.4 q {3}	165.2 dq {34} [2]	b)	Ph: C^1 b); C^2 134.0 d [12]; C^3 128.7 d [11]; C^4 131.0 d [3] py: C^2 150.1; C^3 124.3; C^4 137.2
4	27.2 d [5] (135)	205.2	100.2 q {2—3} (161)	165.2 dq {30} [8]	120.8 dq {282} [8]	Ph: C^1 b); C^2 134.2 d [12]; C^3 128.5 d [10]; C^4 130.8 d [3] Me_2N-py: Me 39.0; C^2 149.1; C^3 106.5; C^4 153.9
5	27.6 d [4] (137)	204.8	99.9 q {2} (160)	165.7 dq {31} [2]	120.6 dq {282} [9]	Ph: C^1 b); C^2 133.7 d [11]; C^3 128.6 d [11]; C^4 130.9 d [3] Me_2-py: Me 25.5; C^2 157.7; C^3 122.3; C^4 137.9
6	27.5 d [4] (137)	205.0	99.9 q {2} (163)	165.6 dq {31} [2]	b)	Tolyl: Me 27.5 d [2], ring-C[c)] Me_2-py: Me 25.5, 25.6; C^2 157.8; C^3 122.2; C^4 137.6
9	24.1 (135)	207.3	101.4 q {2} (161)	164.6 q {31}	120.2 q {281}	Me_2N-py: Me 39.1, 39.2; C^2 151.5, 147.8; C^3 107.9, 106.7; C^4 154.4, 154.1
10[d)]	31.3	b)	b)	b)	b)	bpy: c)
12	22.4 (136)	206.0	101.6 q {2} (163)	164.8 q {32}	120.0 q {281}	Me_2-Phen[e)]: Me 28.6 br, 23.2 br; $C^{1,1'}$ 127.4; $C^{2,2'}$ 126.5 br; $C^{3,3'}$ 137.4; $C^{4,4'}$ b); $C^{5,5'}$ 163.8 br; $C^{6,6'}$ 125.8 br

a) Chemical shifts in ppm from internal Me_4Si. Signals are singlet except those marked with d(doublet), dd(doublet of doublets), q(quartet), and dq(doublet of quartets). Figures in parentheses, brackets, and braces give ^1J(C-H), J(C-P), and J(C-F) in Hz, respectively. b) Indiscernible. c) Not be analyzed. d) In a mixture (1:1 by volume) of $CDCl_3$ and CD_3OD.

c)



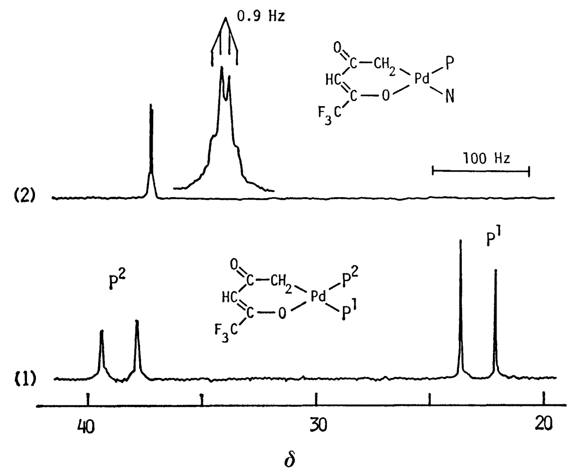


Fig. 1. $^{31}P\{^1H\}$ NMR spectra at 24.2 MHz of [Pd(tfac(2−)-*C,O*)$(PPh_3)_2$] (**2**) (curve 1) and [Pd(tfac(2−)-*C,O*)(PPh_3)(2,6-Me_2-py)] (**5**) (curve 2) in $CDCl_3$ with H_3PO_4 as an external reference.

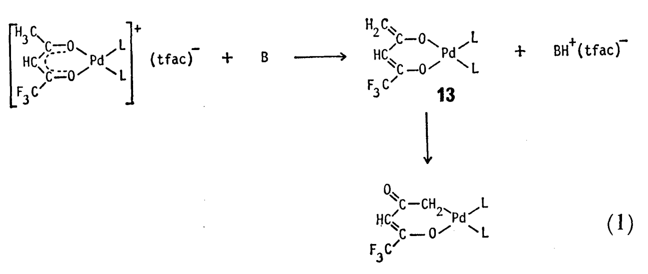
C,O)L_2]. The ^{1}H NMR monitoring revealed that when [Pt(tfac)$_2$] was mixed with a twice molar amount of triphenylphosphine in $CDCl_3$, [Pt(tfac)$(PPh_3)_2$](tfac) was produced at first, which was then converted gradually into [Pt(tfac(2−)-*C,O*)$(PPh_3)_2$].[4b)] The tfac anion in the outer sphere of the salt-like compound was supposed to have abstracted a proton from the methyl group of the chelating tfac anion.

The reaction of [Pd(tfac)$_2$] with twice molar triphenylphosphine in $CDCl_3$ was also confirmed by ^{1}H NMR spectroscopy to form [Pd(tfac)$(PPh_3)_2$](tfac).[4b)] Contrary to the platinum(II) case, however, the palladium(II) complex is stable and deprotonation of the chelating tfac does not occur spontaneously, although exchange of tfac anions in the inner and outer spheres is rapid on the NMR time scale.[4b)] As was described in the Experimental section, addition of a powerful and noncoordinating base, 1,8-bis(dimethylamino)naphthalene ("proton sponge") to the solution of [Pd(tfac)$(PPh_3)_2$](tfac) in dichloromethane was effective for deprotonation of the chelating tfac to give rise to **2**. Employment of pyridine, 4-(dimethylamino)pyridine, and 2,6-dimethylpyridine as a base effected substitution of one phosphine molecule besides deprotonation of the chelating tfac to result in **3**, **4**, and **5**, respectively. The reaction of [Pd(tfac)$_2$] with tris(*o*-tolyl)phosphine produces [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}] reversibly,[4b,22] which also reacts with pyridine derivative (L) to afford **6** and **7**. The latter reactions are also supposed to proceed *via* intermediates of the type [Pd(tfac){P(*o*-tolyl)$_3$}L](tfac).

[Pd(tfac)$_2$] reacts readily with an equimolar amount of 2,2′-bipyridine in benzene at room temperature to afford [Pd(tfac)(bpy)](tfac).[3c] When the product is isolated and dissolved in hot dichloromethane, the salt-like complex is converted into **10**. Therefore the reactions of [Pd(tfac)$_2$] with 2,2′-bipyridine, 1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline in dichloromethane to afford complexes **10**, **11**, and **12** are supposed to proceed *via* similar intermediary salt-like complexes. It is interesting that the bidentate base in **12** is easily displaced by pyridine and its derivatives to give **8** and **9**, for instance. These ligand substitution reactions are convenient for synthesis of **8** and related complexes, since the direct reactions between [Pd(tfac)$_2$] and pyridines attain the following equilibria[3c] and do not give rise to **8** and the like.

$$[\mathrm{Pd(tfac)_2}] \overset{\mathrm{py}}{\rightleftharpoons} [\mathrm{Pd(tfac)(tfac}\text{-}C^3\mathrm{)py}] \overset{\mathrm{py}}{\rightleftharpoons} [\mathrm{Pd(py)_4](tfac)_2}$$

Deprotonation of the chelating tfac monoanion by a base (or tfac itself) might produce a dienediolate complex **13** as an intermediate. Such a dienediolate bonding of acetylacetonate dianion was found in [(η-C$_5$H$_5$)(CO)$_2$Mn{PPh(C$_5$H$_6$O$_2$)}][23] and [(CO)$_5$M{PPh(C$_5$H$_6$O$_2$)}] (M=Cr and W).[24] However, complex **13** seems to be unstable in the case of Pd(II) and Pt(II) compounds, transforming into the C,O-chelate. It should be recalled that deprotonation of [PdCl(CH$_2$COCH$_2$COCH$_3$)(NN)] produced mainly the η^3 complex of acac dianion, [Pd(acac(2−)-C^1—C^3)(NN)], accompanied by a 20—25% amount of [Pd(acac(2−)-*C*,*O*)(NN)] depending on the nature of NN (2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 1,10-phenanthroline), whereas [PdCl(CH$_2$COCH$_2$COOC$_2$H$_5$)(bpy)] gave solely the trihapto complex.[9] These results reflect the tendencies of the three β-dicarbonyl compounds in the keto-enol tautomerization equilibria. Ethyl acetoacetate, which prefers the keto tautomer,[25] forms the η^3-C^1—C^3 complex of its dianion. On the other hand, trifluoroacetylacetone exists almost totally as the enol tautomer[25] and its dianion forms C,O-chelates. Each of the tfac(2−)-C,O-chelates reported in this paper is not contaminated with the trihapto complex. Acetylacetone shows the intermediate behavior.



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(1)

The fact must be added that [Pd(tfac)(PPh$_3$)$_2$]ClO$_4$[26] does not undergo the reaction with nitrogen bases to afford the tfac(2−) chelate. Some kind of cooperation of the tfac anion in the outer sphere might be necessary for deprotonation of the chelating tfac by a nitrogen base. On the other hand the reactions of [Pd(tfac)(PCy$_3$)$_2$](tfac),[4b] where PCy$_3$ abbreviates tricyclohexylphosphine, with nitrogen bases did not afford the tfac(2−) chelate. Trials to prepare [Pd(tfac(2−)-*C*,*O*)(PR$_3$)$_2$] complexes by the reactions of [Pd(tfac)$_2$] with trialkylphosphines such as PEt$_3$ were not successful either. Stronger basicities and/or larger steric demands of PCy$_3$ and PEt$_3$ than PPh$_3$ might be unfavorable for the deprotonation. Although the mechanism is not clear at present, it is worth noting that deprotonation of the chelating tfac anion (Eq. 1) occurs easily under very mild conditions, since dianions of β-dicarbonyl compounds are usually prepared under more severe conditions.[27]

To our knowledge, the first example of the reported β-dik(2−) C,O-chelates is bis(acetylacetonato(2−)-*C*,*O*)selenium(IV). This compound was claimed in patents to have been prepared by the reaction between selenium(IV) oxide and acetylacetone[28] and was used as a brightener in a copper plating bath.[29] The acac(2−) chelates of palladium(II) [Pd(acac(2−)-*C*,*O*)(NN)] could not be isolated either, but characterized only by ^{1}H NMR spectra in solution.[9] On the other hand, the corresponding tfac(2−)-C,O chelates of platinum(II) and palladium(II) were isolated as pure compounds to allow full characterization by NMR spectroscopy, and fortunately single crystals of **5′** suitable for X-ray analysis were obtained.

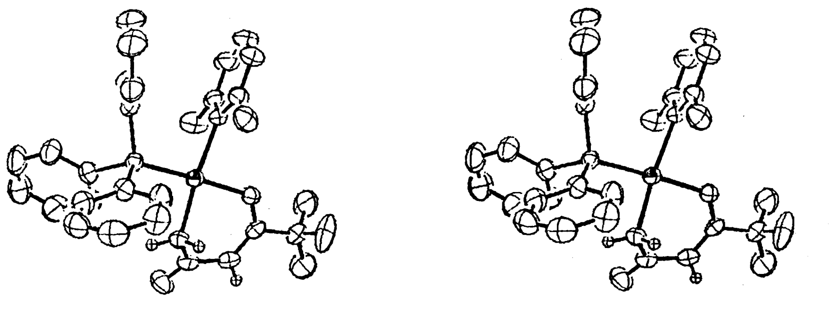

Fig. 2. A stereoscopic view of [Pd(tfac(2−)-*C*,*O*)(PPh$_3$)(2,6-Me$_2$-py)] (**5**) molecule. Non-hydrogen atoms are represented by thermal ellipsoids at 50% probability level. Hydrogen atoms attached only to the α- and γ-carbon atoms of the tfac(2−) dianion are drawn as spheres with the radius of 0.1 Å.

Table 5. Selected bond lengths and bond angles with estimated standard deviations in parentheses

(a) Bond length l/Å			
Pd-C(1)	2.051(4)	C(1)-C(2)	1.481(6)
Pd-O(1)	2.075(3)	C(2)-C(3)	1.458(6)
Pd-P	2.224(1)	C(3)-C(4)	1.360(6)
Pd-N	2.165(3)	C(4)-C(5)	1.512(6)
P-C(11)	1.825(5)	C(4)-O(1)	1.283(5)
P-C(21)	1.827(5)	C(2)-O(2)	1.227(6)
P-C(31)	1.817(5)	C(5)-F(1)	1.307(7)
C(11)-C(12)	1.405(8)	C(5)-F(2)	1.316(6)
C(12)-C(13)	1.367(10)	C(5)-F(3)	1.339(6)
C(13)-C(14)	1.346(13)		
C(14)-C(15)	1.391(12)	N-C(41)	1.345(6)
C(15)-C(16)	1.406(9)	N-C(45)	1.349(6)
C(16)-C(11)	1.408(8)	C(41)-C(42)	1.403(8)
C(21)-C(22)	1.385(7)	C(42)-C(43)	1.382(9)
C(22)-C(23)	1.391(8)	C(43)-C(44)	1.362(9)
C(23)-C(24)	1.368(9)	C(44)-C(45)	1.380(8)
C(24)-C(25)	1.376(8)	C(41)-C(46)	1.524(7)
C(25)-C(26)	1.380(8)	C(45)-C(47)	1.501(8)
C(26)-C(21)	1.379(7)		
C(31)-C(32)	1.396(7)	C(B1)-C(B2)	1.377(12)
C(32)-C(33)	1.394(9)	C(B2)-C(B3)	1.368(12)
C(33)-C(34)	1.376(10)	C(B3)-C(B4)	1.401(13)
C(34)-C(35)	1.358(10)	C(B4)-C(B5)	1.304(13)
C(35)-C(36)	1.365(9)	C(B5)-C(B6)	1.394(14)
C(36)-C(31)	1.393(7)	C(B6)-C(B1)	1.402(13)
(b) Bond angle ϕ/°			
P-Pd-C(1)	87.95(13)	Pd-C(1)-C(2)	112.2(3)
P-Pd-N	96.81(10)	C(1)-C(2)-C(3)	118.3(4)
N-Pd-O(1)	85.40(13)	C(1)-C(2)-O(2)	121.1(5)
O(1)-Pd-C(1)	89.82(15)	C(3)-C(2)-O(2)	120.5(5)
P-Pd-O(1)	177.54(9)	C(2)-C(3)-C(4)	124.2(5)
N-Pd-C(1)	174.54(15)	C(3)-C(4)-O(1)	129.4(4)
		C(3)-C(4)-C(5)	118.7(4)
		C(5)-C(4)-O(1)	111.9(4)
Pd-P-C(11)	112.50(16)	Pd-O(1)-C(4)	122.6(3)
Pd-P-C(21)	111.65(15)	C(4)-C(5)-F(1)	111.8(5)
Pd-P-C(31)	117.58(15)	C(4)-C(5)-F(2)	115.8(5)
C(11)-P-C(21)	105.0(3)	C(4)-C(5)-F(3)	111.6(4)
C(11)-P-C(31)	102.9(3)	F(1)-C(5)-F(2)	106.8(3)
C(21)-P-C(31)	106.1(3)	F(1)-C(5)-F(3)	104.6(4)
		F(2)-C(5)-F(3)	105.5(5)
C(11)-C(12)-C(13)	121.0(6)	Pd-N-C(41)	120.9(3)
C(12)-C(13)-C(14)	120.1(8)	Pd-N-C(45)	119.7(3)
C(13)-C(14)-C(15)	121.4(9)	C(41)-N-C(45)	119.5(4)
C(14)-C(15)-C(16)	120.0(7)	N-C(41)-C(42)	120.3(5)
C(15)-C(16)-C(11)	118.2(6)	N-C(41)-C(46)	118.2(5)
C(16)-C(11)-C(12)	119.2(5)	C(42)-C(41)-C(46)	121.6(5)
C(21)-C(22)-C(23)	121.6(5)	C(41)-C(42)-C(43)	120.0(4)
C(22)-C(23)-C(24)	118.9(6)	C(42)-C(43)-C(44)	118.4(7)
C(23)-C(24)-C(25)	120.0(6)	C(43)-C(44)-C(45)	120.3(6)
C(24)-C(25)-C(26)	121.0(6)	C(44)-C(45)-C(47)	120.8(5)
C(25)-C(26)-C(21)	119.9(5)	N-C(45)-C(44)	121.5(5)
C(26)-C(21)-C(22)	118.5(5)	N-C(45)-C(47)	117.7(5)
C(31)-C(32)-C(33)	118.9(6)	C(B1)-C(B2)-C(B3)	117.5(8)
C(32)-C(33)-C(34)	121.0(7)	C(B2)-C(B3)-C(B4)	122.8(9)
C(33)-C(34)-C(35)	120.0(7)	C(B3)-C(B4)-C(B5)	119.3(9)
C(34)-C(35)-C(36)	120.0(7)	C(B4)-C(B5)-C(B6)	120.7(10)
C(35)-C(36)-C(31)	121.7(6)	C(B5)-C(B6)-C(B1)	119.9(9)
C(36)-C(31)-C(32)	118.3(4)	C(B6)-C(B1)-C(B2)	119.7(8)

Molecular and Crystal Structure of [*Pd*(*tfac*(*2*−)-C,O)(*PPh*$_3$)(*2,6-Me*$_2$*-py*)]·*C*$_6$*H*$_6$ (***5′***). A stereoscopic drawing (*ORTEP* II)[30)] of the **5** molecule is depicted in Fig. 2. Selected bond lengths and bond angles are listed in Table 5. Numbering scheme of atoms in **5** is given in Fig. 3.

The remarkable feature of the structure of **5** molecule is that the palladium atom is C,O-chelated by the tfac(2−) dianion as was expected from the spectroscopic studies (Figs. 2 and 3). The coordination around the palladium atom is essentially square-planar: the Pd atom shows the maximum deviation from the mean plane [0.034(2) Å]. The tfac(2−) dianion is not planar. Two locally planar parts are formed by the C(1), C(2), C(3), and O(2) atoms and by the C(3), C(4), C(5), and O(1) atoms. The dihedral angle between these planes is 29.3(2)°. The tfac(2−) dianion makes a distorted six-membered ring with a central palladium atom. The C(1) atom bonded to the palladium has a distorted sp^3 geometry, bond angles around the C(1) being 112.2(3), 114(3), 97(3), 109(3), 110(3), and 114(4)°. The Pd–C(1) bond length [2.051(4) Å] is consistent with the expected Pd(II)–C(sp^3) bond length and is equal to that (trans to N) in [PdCl(CH$_2$COCH$_2$COOCH$_2$Ph)(py)$_2$] [2.051(8) Å].[8b)] The Pd–C(1) length is also equal to that in [(acac)PdCH$_2$COOH(PPh$_3$)][2.063(4) Å],[31)] but shorter than those in [(PPh$_3$)$_2$Pd{(CH$_2$C=O)$_2$O}][2.124(11) and 2.141(13) Å].[32)] The Pd–O(1) bond length [2.075(3) Å] seems to be equal to those in [(PPh$_3$)Pd(acac)(acac-*C*^{3})][2.048(10) and 2.062(10) Å][5a)] and that in a C,O-chelate, [Pd(C$_2$H$_2$O$_2$)(PPh$_3$)(py)][2.093(11) Å].[33)] The Pd–N bond length [2.165(3) Å] is slightly longer than those in [PdCl(CH$_2$COCH$_2$COOCH$_2$Ph)(py)$_2$][2.120(6) and 2.027(6) Å],[8b)] and also longer than those in [{Pd(acac)(NHEt$_2$)$_2$}$^+$(acac)$^-$][both 2.044(3) Å],[34)] whereas the Pd–N bond length in [Pd(C$_2$H$_2$O$_2$)(PPh$_3$)(py)][2.144(12) Å] seems equal to that in the present complex **5′**. The 2,6-Me$_2$-py ring plane stands approximately normal to the coordination plane, the dihedral angle between these planes being 83.80(15)°.

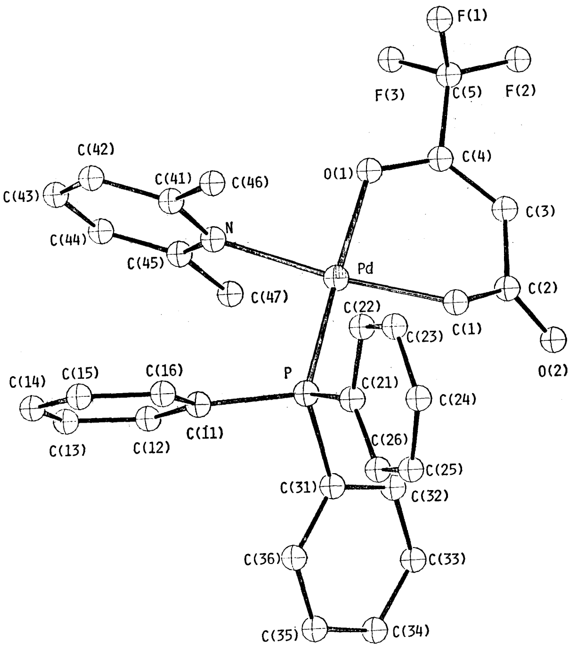

Fig. 3. The numbering scheme of non-hydrogen atoms of the **5** molecule.

TABLE 6. INTERMOLECULAR ATOMIC CONSTANTS[l/Å] LESS THAN 3.5 Å WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

F(1)···C(1)^a	3.457(6)					
F(1)···C(22)^a	3.365(7)	Key:	a,	$1-x$,	$-y$,	$-z$,
C(24)···C(47)^b	3.460(9)		b,	x,	$0.5-y$,	$-0.5+z$,
C(B3)···F(3)^c	3.482(10)		c,	$-x$,	$0.5-y$,	$0.5-z$,
C(B1)···F(2)^d	3.406(9)		d,	$1-x$,	$0.5+y$,	$0.5-z$.

Complex **5′** forms the crystal structure shown in Fig. 4 (*ORTEP* II)[30)] Intermolecular atomic contacts less than 3.5 Å are listed in Table 6. Close contacts are mainly involved between the fluorine atoms of the CF$_3$ group in one molecule and the carbon atoms in the neighboring molecules. The closest distance is F(1) (x, y, z)···C(22) ($1-x$, y, $-z$) [3.365(7) Å].

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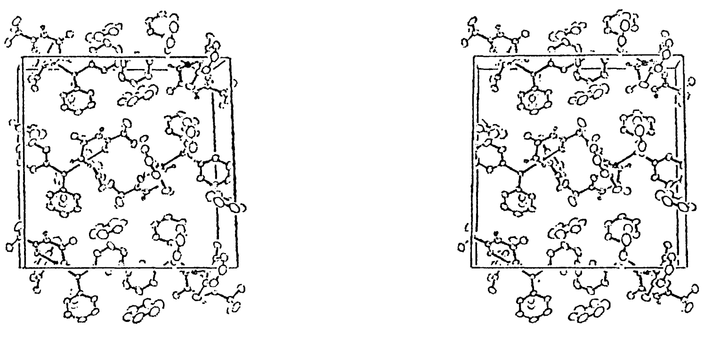

Fig. 4. A stereoscopic view of the crystal structure of [Pd(tfac(2−)-*C*,*O*)(PPh$_3$)(2,6-Me$_2$py)]·C$_6$H$_6$ (**5′**).

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