November, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *3297—3301 (1983)* 3297

The Crystal and Molecular Structure of [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}] Containing an *O*-Unidentate 1,1,1-Trifluoro-2,4-pentanedionate Anion as a Ligand

Shun'ichiro Ooi,* Toshio Matsushita, Kichisuke Nishimoto, Seichi Okeya,† Yukio Nakamura, and Shinichi Kawaguchi*

Faculty of Science, Osaka City Universiry, Sumiyoshi-ku, Osaka 558

†*Faculty of Education, Wakayama University, Masago-cho, Wakayama 640*

(Received May 30, 1983)

The title complex crystallizes in the monoclinic space group C2/c with a=24.900(6) Å, b=8.272(2) Å, c=30.437(9) Å, and β=97.23(2)°. The structure analysis, which converged at R=0.061 and R_w=0.083 with 3017 reflections for which $F_o^2>3\sigma(F_o^2)$, showed that the palladium has a complete square-planar coordination geometry. While one of the tfac ligands is chelating, the other is bound to the metal only through the carbonyl oxygen adjacent to CH_3. The *O*-unidentate tfac ligand lies trans to the CF_3CO moiety of chelating tfac and has a planar structure in which the dangling CF_3CO group is situated trans to the bonding oxygen atom with respect to the C=C bond. The *ab initio* MO calculation for the *Z,Z*-form of the tfac anion indicated that the coordination ability of the acetyl oxygen is higher than that of the trifluoroacetyl oxygen in consistence with the observed structure.

In recent years the reactions of binary and mixed-ligand bis(β-diketonato)palladium(II) and -platinum(II) chelates$^{1)}$ with various nitrogen bases$^{2-4)}$ and tertiary phosphines$^{5)}$ have been studied very extensively. Many types of products were obtained depending on the natures of the central metals, β-diketonate ligands, attacking Lewis bases, and solvents employed. For example, the [Pd(acac)(acac-C^3)L] complexes containing both the *O,O'*-chelated and the central-carbon-bonded 2,4-pentanedionate ligands (acac and acac-C^3, respectively) were afforded by the reactions of [Pd(acac)$_2$] with Lewis bases (L) such as diethylamine, pyridine, and triphenylphosphine as neat liquids and in benzene, respectively.$^{6)}$

The kinetic and equilibrium studies on the reaction of [Pd(acac)$_2$] with various alkylamines in solutions revealed that the carbon-bonded acac complexes are not derived directly from the starting bis-chelate, but resulted *via* the salt-like complexes [Pd(acac)L$_2$](acac).$^{7)}$

$$[\mathrm{Pd(acac)_2}] + 2\mathrm{L} \rightleftharpoons [\mathrm{Pd(acac)L_2}](\mathrm{acac}) \qquad (1)$$

$$[\mathrm{Pd(acac)L_2}](\mathrm{acac}) \rightleftharpoons [\mathrm{Pd(acac)(acac\text{-}}C^3)\mathrm{L}] + \mathrm{L} \qquad (2)$$

In the first stage (Eq. 1) of the overall reaction, one of the chelating acac ligands seems to be displaced *via* the *O*-unidentate state although the intermediate complex [Pd(acac)(acac-*O*)L] was not detected spectrophotometrically in these particular reactions.$^{7)}$

In fact several [M(β-dik)(tfac-*O*)(PR$_3$)]-type complexes (M=Pd^{II} and Pt^{II}; β-dik=acac and tfac; R=ethyl, phenyl, *o*-tolyl, and cyclohexyl) containing the *O*-unidentate 1,1,1-trifluoro-2,4-pentanedionate anion (tfac-*O*) were prepared by the reactions of [M(β-dik)(tfac)] with tertiary phosphines.$^{5)}$ According to the kinetic and equilibrium studies,$^{8)}$ the reaction of [Pd(tfac)$_2$] with tri-*o*-tolylphosphine proceeds reversibly to afford the *O*-unidentate tfac complex exclusively, the equilibrium constant being 1.38×10^3, 4.35×10^3, and more than 10^9 dm^3 mol^{-1} in benzene, dichloromethane, and methanol, respectively, at 25 °C. The steric requirement of P(*o*-tolyl)$_3$ may prevent the formation of [Pd(tfac){P(*o*-tolyl)$_3$}$_2$](tfac) and [Pd(tfac)(tfac-C^3){P(*o*-tolyl)$_3$}].

The *O*-unidentate bonding of the β-diketonate anion was observed first for Me$_2$Si(acac-*O*)$_2$ and Me$_3$Si(acac-*O*)$^{9)}$ followed by [Hg(β-dik-*O*)$_2$] (β-dik=acac, 2,6-dimethyl-3,5-heptanedionate, and 2,2,6,6-tetramethyl-3,5-heptanedionate anions),$^{10)}$ [Pt(acac-*O*)$_2$L$_2$](L=PEt$_3$$^{11)}$ and piperidine$^{12)}$), [Cu(acac)(hfac-*O*)(phen)] (hfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion),$^{13)}$ and [M(CO)$_3${PPh(acac-*O*)$_2$}] (M=Cr and W)$^{14)}$ as well as the above-mentioned [M(β-dik)(tfac-*O*)(PR$_3$)] complexes.$^{5)}$ This paper reports the crystal and molecular structure of [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}] which was determined by the X-ray diffraction method in order to disclose for the first time the *O*-unidentate structure of tfac in a crystal.$^{15)}$

Experimental

The compound was prepared by the reaction of [Pd(tfac)$_2$] with P(*o*-tolyl)$_3$ in hot benzene and an orange plate ($0.09\times0.25\times0.25$ mm^3) for X-ray analysis was obtained on addition of hexane to the solution and spontaneous cooling to room temperature.$^{5)}$ Crystal Data: Monoclinic, a=24.900(6) Å, b=8.272(2) Å, c=30.437(9) Å, β=97.23(2)°, Space group C2/c, D_m=1.52 g cm^{-3}, D_c=1.532 g cm^{-3}, Z=8, μ(Mo $K\alpha$)=7.14 cm^{-1}. The Laue symmetry and the space group were determined from Weissenberg and precession photographs. The unit cell dimension was obtained from the least-squares treatment of 14 θ values of higher angle reflections ($\theta=7-15°$) measured on an automated diffractometer by use of Mo $K\alpha$ radiation.

The intensities were measured on the diffractometer by using the graphite-monochromated Mo $K\alpha$ radiation. The background was counted at each side of the scan range ($\omega=1.0+0.4\tan\theta$), the speed of ω scan being 0.033° s^{-1}. The intensities of three standard reflections monitored every 4 h showed no appreciable variation during the data collection.

Of 3839 independent reflections collected in the $2\theta\leq44°$ range, 3017 with $F_o^2>3\sigma(F_o^2)$ were used for the structure determination. The crystal structure was solved by the heavy atom technique. The positional and thermal parameters were refined by block-diagonal-matrix least-squares to R 0.061, R' $(=[\sum w\Delta^2/\sum wF_o^2]^{1/2})$ being 0.083. The minimized function was $\sum w(F_o-|F_c|)^2$, where $w=1/\sigma^2(F_o)$. No attempt was made to locate hydrogen atoms. In the course

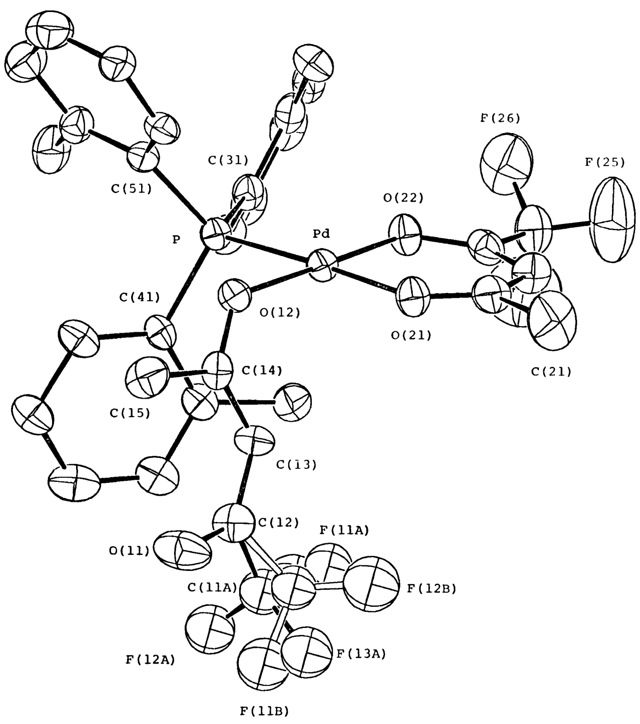


Fig. 1. ORTEP drawing of [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}]. Thermal ellipsoids are drawn at 30% probability level. The CF$_3$ group composed of C(11), F(11), F(12), and F(13) is twofold disordered.

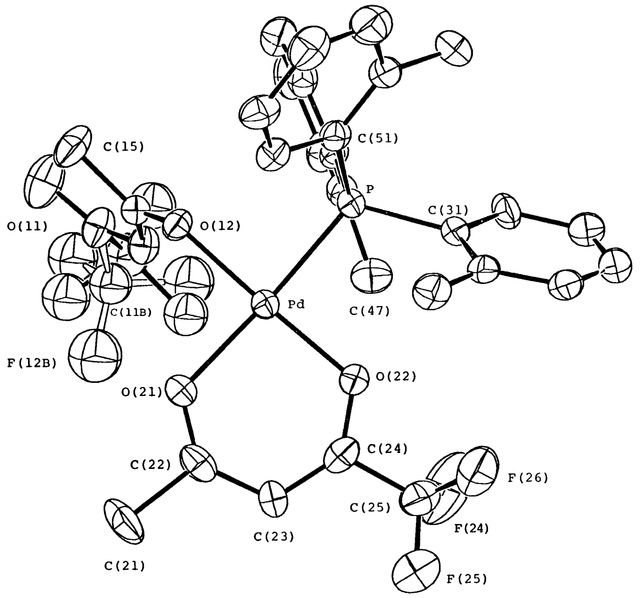


Fig. 2. Projection of the complex along the normal of coordination plane. Thermal ellipsoids are drawn at 30% probability level.

of the structure analysis, one of the CF$_3$ groups was found to be in disorder. The electron density distribution for this group was best interpreted by the model (twofold disorder) shown in Figs. 1 and 2. Occupancies for the disordered CF$_3$ groups were assumed to be equal. All parameter shifts in the final cycle of the refinement were less than 0.5σ except for the atomic parameters of the disordered CF$_3$ group, for which the shifts were in the 0.15σ−1.5σ range.

Table 1. Fractional coordinates and temperature factors for [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}]. Standard deviations of the least significant figures are given in parentheses

Atom	x	y	z	B_{eq}/Å^2
Pd	0.10819(3)	0.1369(1)	0.15603(2)	3.60(2)
P	0.1351(1)	0.0126(3)	0.0967(1)	3.5(1)
C(31)	0.2020(4)	-0.080(1)	0.1062(3)	3.9(3)
C(32)	0.2481(4)	0.023(1)	0.1163(3)	4.8(3)
C(33)	0.2991(4)	-0.054(2)	0.1208(3)	5.5(4)
C(34)	0.3034(5)	-0.221(2)	0.1160(3)	6.2(4)
C(35)	0.2585(5)	-0.318(1)	0.1066(3)	6.0(4)
C(36)	0.2075(4)	-0.245(1)	0.1009(3)	4.7(3)
C(37)	0.2450(4)	0.205(1)	0.1220(4)	5.5(3)
C(41)	0.0850(3)	-0.148(1)	0.0824(3)	3.7(3)
C(42)	0.0752(4)	-0.269(1)	0.1120(3)	4.3(3)
C(43)	0.0344(4)	-0.377(1)	0.1006(4)	5.3(3)
C(44)	0.0008(5)	-0.364(1)	0.0599(4)	6.4(4)
C(45)	0.0081(4)	-0.239(1)	0.0297(4)	5.6(4)
C(46)	0.0519(4)	-0.132(1)	0.0424(4)	4.9(3)
C(47)	0.1075(5)	-0.290(1)	0.1586(3)	5.5(3)
C(51)	0.1368(3)	0.149(1)	0.0495(3)	3.8(3)
C(52)	0.1558(4)	0.101(1)	0.0108(3)	4.7(3)
C(53)	0.1585(5)	0.218(2)	-0.0235(4)	6.9(4)
C(54)	0.1451(5)	0.385(2)	-0.0150(4)	7.0(4)
C(55)	0.1262(4)	0.430(1)	0.0244(3)	5.5(3)
C(56)	0.1215(4)	0.311(1)	0.0558(3)	4.2(3)
C(57)	0.1742(5)	-0.066(2)	0.0008(4)	6.4(4)
O(21)	0.0790(3)	0.2534(8)	0.2072(2)	4.6(2)
O(22)	0.1753(2)	0.0676(8)	0.1930(2)	4.6(2)
C(21)	0.0745(6)	0.353(2)	0.2816(5)	9.3(6)
C(22)	0.1037(4)	0.254(1)	0.2465(3)	5.2(3)
C(23)	0.1526(4)	0.178(1)	0.2630(3)	5.1(3)
C(24)	0.1823(4)	0.093(1)	0.2358(3)	4.8(3)
C(25)	0.2329(5)	0.007(2)	0.2567(4)	6.8(4)
F(24)	0.2234(5)	-0.148(1)	0.2598(4)	16.4(5)
F(25)	0.2507(4)	0.056(2)	0.2953(3)	15.3(5)
F(26)	0.2741(3)	0.016(1)	0.2333(3)	10.9(3)
O(11)	-0.1094(3)	-0.032(1)	0.1267(3)	8.3(3)
O(12)	0.0409(2)	0.2037(8)	0.1167(2)	4.0(2)
C(15)	-0.0501(4)	0.209(2)	0.0849(4)	6.5(4)
C(14)	-0.0051(4)	0.138(1)	0.1186(3)	4.1(3)
C(13)	-0.0154(4)	0.016(1)	0.1469(3)	4.4(3)
C(12)	-0.0658(4)	-0.058(1)	0.1483(4)	5.3(3)
C(11A)	-0.068(1)	-0.219(4)	0.1721(9)	7.5(7)
F(11A)	-0.0201(6)	-0.250(2)	0.2013(5)	7.7(4)
F(12A)	-0.0796(6)	-0.341(2)	0.1503(5)	8.6(4)
F(13A)	-0.1058(6)	-0.205(2)	0.2034(5)	9.2(4)
C(11B)	-0.068(1)	-0.172(3)	0.1874(9)	7.0(7)
F(11B)	-0.1153(7)	-0.252(2)	0.1830(5)	9.7(4)
F(12B)	-0.0580(7)	-0.115(2)	0.2265(6)	11.2(5)
F(13B)	-0.0311(7)	-0.292(2)	0.1851(5)	10.3(4)

The atomic scattering factors with correction for anomalous dispersion of the metal atom were taken from Ref. 16. The atomic coordinates are given in Table 1. The F_o—F_c table and the anisotropic thermal parameters are preserved at the Chemical Society of Japan (Document No. 8347). The computation was performed by a FACOM 230-60 computer at Osaka City University and an ACOS-700 computer at the Crystallographic Research Center of Osaka University by use of the programs in the UNICS[17)] and ORTEP.[18)]

Results and Discussion

Figures 1 and 2 show the perspective view of the molecule and its projection along the normal of the coordination plane, respectively. Figure 3 gives the view of the P(*o*-tolyl)$_3$ ligand along the M–P vector. Bond lengths and angles are summarized in Table 2. Average values are given for the parameters of CF$_3$ groups, since these groups have large thermal parameters indicative of a disorder (Table 1) and hence individual structural parameter is of less importance.

The Pd atom lies on a complete plane comprised of 3O and P atoms (Table 3). While one of the two tfac ligands is *O*,*O*′-chelated in the usual fashion, the other is linked to the metal atom only through the acetyl oxygen atom. Of the two Pd–O bonds constructing the chelate ring, the Pd–O(21) bond is more

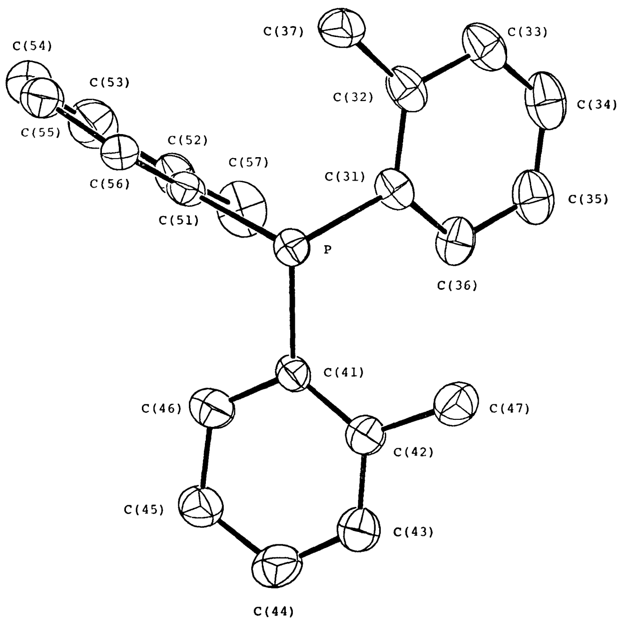


Fig. 3. The structure (30% ellipsoids) of the P(*o*-tolyl)$_3$ ligand viewed along the Pd–P vector.

TABLE 2. BOND LENGTHS AND ANGLES

Bond length	l/Å	Bond length	l/Å
Pd-P	2.251(3)	P-C(31)	1.822(9)
-O(12)	2.011(6)	-C(41)	1.836(9)
-O(21)	2.041(7)	-C(51)	1.834(10)
-O(22)	1.979(6)		
C(11)-C(12)	A 1.52(3) B 1.53(3)	C(21)-C(22)	1.593(19)
C(12)-O(11)	1.217(12)	C(22)-O(21)	1.276(12)
C(12)-C(13)	1.403(14)	C(22)-C(23)	1.406(14)
C(13)-C(14)	1.372(14)	C(23)-C(24)	1.371(15)
C(14)-O(12)	1.274(11)	C(24)-O(22)	1.308(12)
C(14)-C(15)	1.538(14)	C(24)-C(25)	1.512(15)
C(11)-F	1.35[a)]	C(25)-F	1.32[c)]

Bond angle	ϕ/°	Bond angle	ϕ/°
O(21)-Pd-O(22)	93.4(3)	Pd-P-C(31)	115.0(3)
P-Pd-O(12)	87.6(2)	Pd-P-C(41)	105.0(3)
P-Pd-O(22)	90.5(2)	Pd-P-C(51)	112.6(3)
Pd-O(12)-C(14)	122.8(6)	C(31)-P-C(41)	108.3(4)
Pd-O(21)-C(22)	122.8(7)	C(31)-P-C(51)	105.8(4)
Pd-O(22)-C(24)	121.1(6)	C(41)-P-C(51)	110.0(4)
C(11)-C(12)-C(13)	A 119(1) B 115(1)	C(21)-C(22)-C(23)	116.1(9)
C(11)-C(12)-O(11)	A 110(1) B 115(1)	C(21)-C(22)-O(21)	115.0(9)
C(13)-C(12)-O(11)	130.1(11)	C(23)-C(22)-O(21)	128.8(10)
C(12)-C(13)-C(14)	125.5(9)	C(22)-C(23)-C(24)	121.5(9)
C(13)-C(14)-O(12)	125.6(8)	C(23)-C(24)-O(22)	132.0(9)
C(15)-C(14)-O(12)	112.9(8)	C(25)-C(24)-O(22)	110.1(9)
C(15)-C(14)-C(13)	121.5(9)	C(25)-C(24)-C(23)	117.9(9)
C(12)-C(11)-F	113[b)]	C(24)-C(25)-F	113[d)]
F-C(11)-F	106[b)]	F-C(25)-F	106[d)]

a) Mean value of six C(11)-F distances. b) Mean value of six C-C-F or F-C-F angles. c) Mean value of three C(25)-F distances. d) Mean value of three C-C-F or F-C-F angles.

TABLE 3. ATOM DEVIATION FROM MEAN PLANE AND INTERPLANAR ANGLE

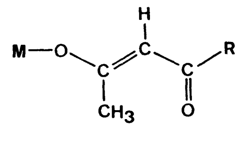
Atom deviation	d/Å
Plane 1	[O(12), O(21), O(22), P] Pd, 0.002(3); O(12), 0.003(7); O(21), −0.003(7); O(22), 0.003(7); P, −0.003(4)
Plane 2	[O(11), O(12), C(12), C(13), C(14), C(15)] O(11), −0.003(12); O(12), −0.009(8); C(12), −0.005(14); C(13), 0.009(13); C(14), 0.005(13); C(15), 0.003(14); C(11A), −0.37(3); C(11B), 0.22(3)
Plane 3	[O(21), O(22), C(21), C(22), C(23), C(24), C(25)] O(21), −0.058(9); O(22), 0.055(9); C(21), 0.032(17); C(22), −0.006(15); C(23), 0.006(15); C(24), 0.016(14); C(25), −0.045(15)

Interplanar angle	φ/°
Plane 1-Plane 2	74.8(4)
[Pd, O(21), O(22)] plane-Plane 3	175.3(4)

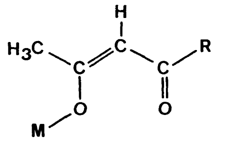
than 0.06 Å longer than the other Pd–O(22) bond probably owing to the trans influence of the tertiary phosphine ligand. The unidentate tfac enolate ligand has a planar structure in which the dangling CF$_3$CO group lies trans to the bonding oxygen around the C=C bond, the torsion angle between the C(14)–C(15) and C(12)–O(11) bonds being 1.1°. The electron density due to the disordered CF$_3$ group is best interpreted by the model shown in Fig. 1. The C(12)–C(11A) and C(12)–C(11B) bonds make angles 13.1° and 9.4°, respectively, with the [O(11), C(12), C(13)] plane.

Since the chelating tfac ligand is unsymmetric, two geometrical arrangements around the metal atom are conceivable for this complex even if the unidentate tfac ligand is bound to the metal exclusively through the acetyl oxygen. In fact the two isomers exist in equilibrium in CDCl$_3$ and the present isomer (*trans*-[P,O(21)]) is overwhelmingly abundant (>80%) at ambient temperature.[5)] As may be imagined from Fig. 2, there exists no severe atom overcrowding in the *cis*-[P,O(21)] isomer either and hence the higher stability of the *trans*-[P,O(21)] isomer seems to stem from some electronic origin. The σ-donating ability of the CH$_3$CO moiety of the chelating tfac is higher than that of the CF$_3$CO moiety (*vide infra*) and may strengthen the Pd-phosphine π-bonding.[5)]

The planar *O*-unidentate β-diketonate ligand may have either the trans or cis configuration with respect to the C=C bond. By the ^{1}H NMR studies Pinnavaia and his collaborators found that the R$_3$Si(acac-*O*) complexes are composed of cis and trans isomers in



trans

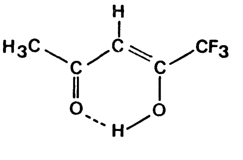


cis

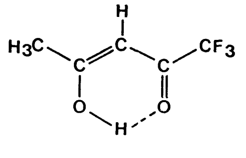
equilibrium and the former is fluxional undergoing the head-to-tail coordinating atom exchange in solution.[19] On the other hand, the acac anions involved in $[Pt(acac\text{-}O)_2(PEt_3)_2]$[11] and $[Pt(acac\text{-}O)_2(\text{piperidine})_2]$[4] have the cis configuration exclusively, exhibiting no fluxional motion. The cis configurations of acac in $[Cr(CO)_5\{PPh(acac\text{-}O)_2\}]$[14] and of hfac in [Cu(acac)(hfac-*O*)(phen)][13] were confirmed by X-ray analysis. The ^1H NMR spectrum of the present complex in $CDCl_3$ also indicated that the *O*-unidentate tfac ligand has the cis configuration[5] in contradiction with the present X-ray structure. The discrepancy between the structures in solution and a crystal can not be reasonably rationalized.

The *O*-unidentate tfac ligand should have a greater contribution from the structure $^-O\text{-}C(CH_3)\text{=}CH\text{-}C(CF_3)\text{=}O$, but no evidence for the π electron localization can be detected. Thus, although the C(12)–O(11) distance is shorter than the C(14)–O(12) distance (Table 2), it can not be the conclusive evidence for the π electron localization since (i) the thermal parameter is larger for O(11) than for O(12) and (ii) no significant difference exists between the C(12)–C(13) and C(13)–C(14) distances. On the contrary, the coplanar disposition of the O(12), C(14), C(15), C(13), C(12), and O(11) atoms is suggestive of some extent of π electron delocalization (Table 3). The nonbonded O(11)···C(15) distance (2.87(2) Å) is noteworthy, since it is considerably shorter than the value expected from the van der Waals radii of the components. Although the unidentate and bidentate tfac ligands differ in configuration, there is no remarkable difference between the corresponding structural parameters.

The enol tautomers of acacH[20] and hfacH[21] in gas phase were found by the electron diffraction method to have the planar symmetric hydrogen-chelate structure.[22] On the other hand, neutron diffraction data confirmed that the enol molecule of 1,3-diphenyl-1,3-propanedione has an asymmetric intramolecular hydrogen bond, the difference in the two O–H bond lengths being 0.199(17) Å.[25] The enol molecule of tfacH should certainly have an asymmetric hydrogen-chelate structure (A) or (B).

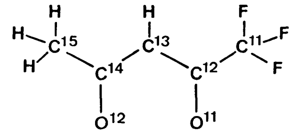


(A)



(B)

Takeuchi and his collaborators compared the ^{13}C chemical shifts of the carbonyl carbons in tfacH in several solvents.[26] The intramolecular hydrogen bond retained in nonpolar solvents was supposed to be cleaved in dimethyl sulfoxide (DMSO-d_6) to form an intermolecular hydrogen bond. The signal from the carbonyl carbon adjacent to CH_3 showed a marked upfield shift (5.2 ppm) in DMSO-d_6 as compared with that in $CDCl_3$, while the chemical shift of the carbonyl carbon adjacent to CF_3 showed a minor difference (1.0 ppm) in these solvents. Based on this observation, Takeuchi *et al.* concluded that tfacH has structure (A) rather than (B) in nonpolar solvents.[26] If this structure assignment is correct, the proton affinity of the trifluoroacetyl oxygen (O(11)) must be higher than that of the acetyl oxygen (O(12)), and the tfac anion may be expected to be bound to a metal atom through O(11) when it serves as a unidentate ligand. The coordination mode found for the present complex is contrary to this expectation, the tfac anion being bound to palladium through O(12).



Coordination ability of the oxygen atom in a substituted 2,4-pentanedionate anion is enhanced with increase of the negative net charge on the donor atom, and also with increase of the square of AO coefficient at the oxygen in the σ-type HOMO. These values were calculated by the *ab initio* MO method with the STO-3G minimal base set and the results obtained are shown in Table 4. The negative net charge on either of oxygen atoms in the tfac anion is smaller than that in acac in accordance with higher acidity of tfacH than acacH.[28] In the tfac anion, both the negative charge and AO coefficient in the σ-type HOMO are larger on O(12) than on O(11), indicating that the coordination ability of the acetyl oxygen is higher than that of the trifluoroacetyl oxygen. These results are consistent with the unidentate structure of tfac in Pd^{II} and Pt^{II} complexes observed in crystals and solution.

Table 4. The net charge and AO coefficient in the σ-type HOMO at the oxygen atoms in the 2,4-pentanedionate and 1,1,1-trifluoro-2,4-pentanedionate anions of the *Z,Z*-form[a]

	Net charge on		AO coefficient in the σ-type HOMO at	
	O(11)	O(12)	O(11)	O(12)
acac	−0.374	−0.374	0.6577	0.6577
tfac	−0.346	−0.357	0.6179	0.6847

a) The following geometrical parameters[27] were used in the *ab initio* calculation for the tfac anion; bond lengths (Å): $r(C(11)\text{-}C(12))=r(C(14)\text{-}C(15))=1.51$, $r(C(12)\text{-}C(13))=r(C(13)\text{-}C(14))=1.40$, $r(C(12)\text{-}O(11))=r(C(14)\text{-}O(12))=1.28$, $r(C(13)\text{-}H)=1.08$, $r(C(15)\text{-}H)=1.09$, $r(C(11)\text{-}F)=1.38$; bond angles: CCC=CCO=HC(13)C=120°, HCH=FCF=109.47°

References

1) a) S. Okeya and S. Kawaguchi, *Inorg. Synth.*, **20**, 65 (1980); b) S. Okeya, S. Ooi, K. Matsumoto, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1085 (1981).

2) S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1978 (1981).

3) S. Okeya, H. Yoshimatsu, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **55**, 483 (1982).

4) S. Okeya, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **55**, 1460 (1982).

5) S. Okeya, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 3396 (1981).

6) S. Baba, T. Ogura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 665 (1974).

7) S. Matsumoto and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **53**, 1577 (1980).

8) S. Matsumoto and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1704 (1981).

9) R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

10) G. S. Hammond, D. C. Nonhebel, and C.-H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963); D. C. Nonhebel, *J. Chem. Soc.*, **1963**, 738.

11) T. Ito, T. Kiriyama, and A. Yamamoto, *Chem. Lett.*, **1976**, 835.

12) S. Okeya, F. Egawa, Y. Nakamura, and S. Kawaguchi, *Inorg. Chim. Acta*, **30**, L319 (1978).

13) N. A. Bailey, D. E. Fenton, M. V. Franklin, and M. Hall, *J. Chem. Soc.*, *Dalton Trans.*, **1980**, 984.

14) J. von Seyerl, D. Neugebauer, G. Huttner, C. Kruger, and Y.-H. Tsay, *Chem. Ber.*, **112**, 3637 (1979).

15) A short communication appeared in S. Ooi, T. Matsushita, K. Nishimoto, Y. Nakamura, S. Kawaguchi, and S. Okeya, *Inorg. Chim. Acta*, **76**, L55 (1983).

16) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

17) "UNICS," The Crystallographic Society of Japan, Tokyo (1969).

18) C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1976).

19) J. J. Howe and T. J. Pinnavaia, *J. Am. Chem. Soc.*, **91**, 5378 (1969); T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *ibid.*, **92**, 4544 (1970).

20) A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *J. Am. Chem. Soc.*, **93**, 6399 (1971).

21) A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Am. Chem. Soc.*, **93**, 1148 (1971).

22) Egan *et al.* determined the selected ^{13}C and ^{2}H spin-lattice relaxation times for the enol form of acacH and its perdeuterated analogue and concluded that the intramolecular hydrogen bond in the enolic acacH is of the double minimum type.[23)] Brown reported on the basis of the X-ray photoelectron spectroscopic data that the two oxygen atoms in hfacH are inequivalent by virtue of an asymmetric hydrogen bond.[24)]

23) W. Egan, G. Gunnarsson, T. E. Bull, and S. Forsén, *J. Am. Chem. Soc.*, **99**, 4568 (1977).

24) R. S. Brown, *J. Am. Chem. Soc.*, **99**, 5497 (1977); R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *ibid.*, **101**, 3157 (1979).

25) R. D. G. Jones, *Acta Cryst.*, *Sect. B*, **32**, 1807 (1976).

26) J. Niwa, M. Yamazaki, and T. Takeuchi, *Chem. Lett.*, **1975**, 707; C. Shibata, T. Takeuchi, M. Yamazaki, and J. Niwa, *Nippon Kagaku Kaishi*, **1978**, 836.

27) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement. The Chemical Society, London (1965).

28) T. Sekine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nucl. Chem.*, **35**, 3968 (1973).