

The O-Unidentate Structure of a Trifluoroacetylacetonate Anion in Pd(tfac)(tfac-O){P(*o*-tolyl)₃}

SHUN'ICHIRO OOI, TOSHIO MATSUSHITA, KICHISUKE NISHIMOTO, YUKIO NAKAMURA, SHINICHI KAWAGUCHI

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

and SEICHI OKEYA

Faculty of Education, Wakayama University, Wakayama 640, Japan

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Monoanions of acetylacetonate(acacH) and other β -dicarbonyl compounds (β -dikH) are very popular ligands [1], usually forming chelates with almost all metal ions [2]. The O-unidentate bonding of the β -dik anions was observed firstly for the di-methylsilyl and trialkylsilyl acetylacetonates [3] followed by mercury(II) [4], platinum(II) [5–7], gold(III) [8], phosphorus [9], copper(II) [10], and palladium(II) [7, 11] compounds. This communication reports the molecular structure of (trifluoroacetylacetonato-O, O') (trifluoroacetylacetonato-O){tris(*o*-tolyl)phosphine}palladium(II), Pd(tfac)(tfac-O){P(*o*-tolyl)₃} (*I*) [7, 12], which presents the first example of the O-unidentate structure of tfac determined by X-ray analysis, revealing two novel features: (i) bonding to the metal atom through the acetyl oxygen and (ii) dangling of the trifluoroacetyl group trans to the bonding oxygen atom around the C=C bond.

Although the acac enolate anions in R₃Si(acac-O) are composed of *cis* and *trans* isomers in equilibrium, and the former is fluxional undergoing the head-to-tail coordinating-atom exchange in solution [13], the acac anions involved in Pt(acac-O)₂(PEt₃)₂ [5] and Pt(acac-O)₂(piperidine)₂ [6] have the *cis* configuration exclusively, showing no fluxional motion. The *cis* configuration of acac in Cr(CO)₅{PPh(acac-O)₂} [9] and Cu(acac)(hfac-O)(phen) [10] was confirmed by X-ray analysis. The tfac anions in Pt(tfac-O)₂L₂ (L = Et₂NH, piperidine, PEt₃, and PCy₃) [6b, 7] and Pt(tfac)(tfac-O){P(*o*-tolyl)₃} [7] are linked with platinum via the acetyl oxygen atom, as evidenced by the ¹H–¹⁹⁵Pt coupling. In order to reveal the coordination structure of the O-unidentate tfac anion, X-ray analysis of complex *I* was carried out [14] and its molecular structure is shown in Fig. 1. Crystal Data: Monoclinic, *a* = 24.900(6) Å, *b* = 8.272(1) Å, *c* = 30.437(1) Å, β = 97.23(1)°, Space group C2/c, *Z* = 8, μ (Mo K α) = 7.83 cm⁻¹. Intensity data were measured on an automated diffractometer by use of Mo K α radiation. Of 3839 independent reflec-

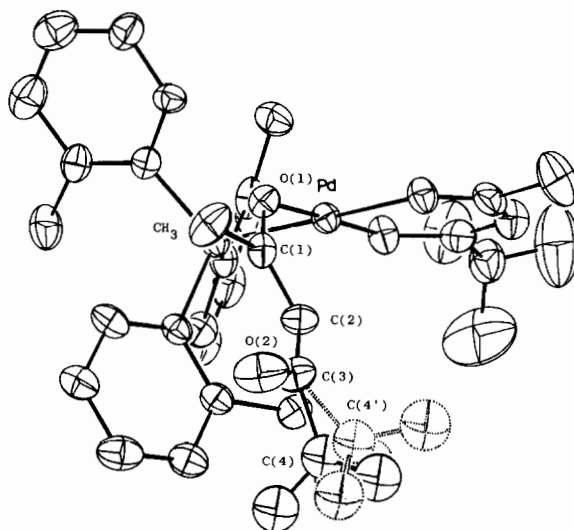


Fig. 1. ORTEP drawing of Pd(tfac)(tfac-O){P(*o*-tolyl)₃} (*I*).

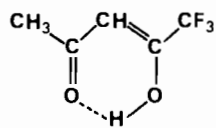
tions collected in the $2\theta \leq 44^\circ$ range, 3017 with $F_0^2 > 3\sigma(F_0^2)$ were used for the structure determination. The structure was solved by the heavy-atom technique and refined by the least-squares to R 0.061. No attempt was made to locate H atoms. Anisotropic thermal parameters were used for all but one CF₃ group found to have a disorder (Fig. 1). Occupancy was assumed to be equal for the groups shown by full and dotted circles.

The Pt atom has a square-planar coordination by 3O and P atoms. The Pd–O bond (2.041(7) Å), in which the O atom is trans to P, is *ca.* 0.03 Å longer than the other two Pd–O bonds (1.979(7) and 2.011(7) Å). Such an elongation of Pd–O bond was also observed in Pd(hfac)₂{P(*o*-tolyl)₃} [15] and should be ascribed to the trans influence of the phosphine ligand. While one of the tfac ligands is bidentate forming a planar six-membered chelate ring, the other is unidentate and only the carbonyl oxygen atom adjacent to the methyl group participates in coordination with the Pd atom. The unidentate tfac ligand has a trans planar structure, the torsion angle between C(1)–CH₃ and C(3)–O(2) bonds being 1.1°. The electron density due to the disordered CF₃ group is best interpreted by the model shown in Fig. 1. The C(3)–C(4) and C(3)–C(4') bonds make angles of 13.1° and 9.4° with the [C(2), C(3), O(2)] plane, respectively. Owing to the disorder, the accuracy of the structural parameters is not high enough to allow a discussion on the π electron distribution in the unidentate tfac ligand. The molecular parameters in the bidentate tfac and phosphine ligands are normal.

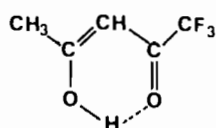
Since the tfac anion is unsymmetric, two geometrical arrangements around the metal atom are conceivable for complex *I* even though the unidentate

tfac is bound preferentially through the acetyl oxygen. The isomer of which the molecular structure was determined is thermodynamically more stable and more abundant (>80%) in CDCl_3 than the other isomer [7]. It is worth noting that the O-unidentate tfac has the trans configuration around the $\text{C}=\text{C}$ bond with no bonding interaction between the CF_3CO moiety and palladium, whereas the corresponding hexafluoroacetylacetonate complex $\text{Pd}(\text{hfac})_2\{\text{P}(o\text{-tolyl})_3\}$ [15] as well as $\text{Pt}(\text{hfac})_2(\text{PCy}_3)$ [15] and $[\text{Pd}(\text{hfac})(\text{triphos})](\text{hfac})$ (triphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2$) [16] has the distorted square-pyramidal structure, one of the oxygen atoms effectively occupying the apical position. The bidentate behavior of the symmetric hfac anion may be stimulated by the chelate and electron-delocalization effects, although hfac is less basic than tfac [17]. The tfac anion, on the other hand, is unsymmetric and the charge density may be larger on the acetyl oxygen atom than on the trifluoroacetyl oxygen, making the O-unidentate bonding less unfavorable, especially in the presence of an appropriate ancillary ligand. The equilibrium constant of the reaction $\text{Pd}(\text{tfac})_2 + \text{P}(o\text{-tolyl})_3 \rightleftharpoons I$ was reported to be 1.38×10^3 , 4.35×10^3 , and larger than $10^9 \text{ dm}^3 \text{ mol}^{-1}$ at 25°C in benzene, dichloromethane, and methanol, respectively [12]. Steric requirement of $\text{P}(o\text{-tolyl})_3$ seems to prevent formation of $[\text{Pd}(\text{tfac})\text{L}_2](\text{tfac})$ and $\text{Pd}(\text{tfac})(\text{tfac}-\text{C}^3)\text{L}$ ($\text{L} = \text{P}(o\text{-tolyl})_3$).

Takeuchi and his co-workers [18] preferred structures 2 and 3 for the enol molecule of tfacH, based on the ^{13}C NMR observation that the signal for the carbonyl carbon adjacent to CH_3 showed remarkable upfield shift (5.2 ppm) in $\text{DMSO}-d_6$ as compared with that in CDCl_3 , while the signal for the CO carbon adjacent to CF_3 showed a minor shift (1.0 ppm) in these solvents. This proposal is not consistent with the O-unidentate structure of tfac in the present complex.



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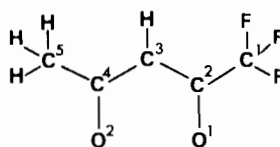
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Coordination ability of the oxygen atom in a substituted acetylacetonate anion is enhanced with increase of the negative net charge on the donor atom, and also with increase of the absolute value of AO coefficient at the oxygen in the σ -type HOMO. These values were calculated by the ab initio MO method with the STO-3C minimal basis set and the results obtained are shown in Table I. The negative net charge on either of oxygen atoms in the tfac anion is smaller than that in acac in accordance with

TABLE I. The Net Charge and AO Coefficient in the σ -Type HOMO at the Oxygen Atoms in the Acetylacetonate and Trifluoroacetylacetonate Anions^a.

	Net charge on		AO coefficient in the σ -type HOMO at	
	O ¹	O ²	O ¹	O ²
acac	-0.374	-0.374	0.6577	0.6577
tfac	-0.346	-0.357	0.6179	0.6847

^aThe following geometrical parameters [19] were used in the ab initio MO calculation for the Z,Z-form of the tfac anion; bond distances (\AA): $r(\text{C}^1-\text{C}^2) = r(\text{C}^4-\text{C}^5) = 1.51$, $r(\text{C}^2-\text{C}^3) = r(\text{C}^3-\text{C}^4) = 1.40$, $r(\text{C}^2-\text{O}^1) = r(\text{C}^4-\text{O}^2) = 1.28$, $r(\text{C}^3-\text{H}) = 1.08$, $r(\text{C}^5-\text{H}) = 1.09$, $r(\text{C}^1-\text{F}) = 1.38$; bond angles: $\text{CCC} = \text{CCO} = \text{HC}^3\text{C} = 120^\circ$, $\text{HCH} = \text{FCF} = 109.47^\circ$.



the lower basicity of the former [17]. In the tfac anion, both the negative charge and AO coefficient in the σ -type HOMO are larger on O² than on O¹, 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 observed both in crystals and solution.

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