Bis(β-diketonato)-palladium(II) and -platinum(II) Complexes

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A number of palladium(II) and platinum(II) bis-chelates have been prepared which contain one kind of symmetric or unsymmetric β-diketonate anions, or involve two different β-diketonate anions. Existence of the *cis* and *trans* isomers in solution of the binary chelates of unsymmetric β-diketones was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Geometrical isomerization of the palladium(II) complexes to attain equilibrium in solution is fast, while the platinum(II) complexes are quite inert. The mixed-ligand chelates are stable in solution, showing no sign of disproportionation. The isomeric pairs of bis(1-phenyl-1,3-butanedionato)palladium(II), bis(2,4-hexanedionato)palladium(II), and bis(1,1,1-trifluoro-2,4-pentanedionato)platinum(II) were isolated, and molecular structure of the *cis* isomer of the first complex was determined by X-ray analysis.

2,4-Pentanedione and other β-dicarbonyl compounds (β-dikH) react with a wide variety of metal ions to form the (O,O′) chelates[1] of the $[M(\beta\text{-dik})_n]$ type which are soluble in organic solvents, and are used frequently as analytical reagents. These complexes are useful not only for comparative studies of various metal ions, but also as starting materials for preparation of organometallic compounds and as catalysts for organic syntheses. Thus a huge number of papers have appeared concerning the complexes containing β-dicarbonyl compounds as a ligand.[2]

Although optical and geometrical isomerization of the octahedral $[M(\beta\text{-dik})_3]$ and related complexes have been studied extensively,[3] investigations on geometrical isomerism of the square-planar $[M(\beta\text{-dik})_2]$ complexes containing unsymmetrical β-dicarbonyl compounds are rather few. Recently two of the present authors have prepared bis(1-ethoxy-1,3-butanedionato)palladium(II) and showed that it exists as an equilibrium mixture of *cis* and *trans* isomers in chloroform.[4] This paper is concerned with preparation and spectroscopic studies of a number of palladium(II) and platinum(II) complexes of symmetric and unsymmetric β-dicarbonyl compounds including several mixed-ligand bis-chelates. A preliminary report on isolation of *cis*- and *trans*-bis(1-phenyl-1,3-butanedionato)palladium(II) and X-ray structure of the *cis* isomer was published in a short communication,[5] and the full account will be included in this paper.

Experimental

Preparation of Complexes. The palladium(II) and platinum(II) chelates of β-dicarbonyl compounds were prepared by one of the following four methods. (A) To an aqueous solution of sodium tetrachloropalladate(II), $Na_2[PdCl_4]$, was added more than twice moles of a ligand together with an appropriate amount of base. (B) Mercury(II) perchlorate and/or silver(I) perchlorate was added to $Na_2[PdCl_4]$ or potassium tetrachloroplatinate(II), $K_2[PtCl_4]$, in aqueous solution to prepare $[M(H_2O)_4]^{2+}$ ions *in situ*, which were allowed in turn to react with a sodium or potassium salt of the β-dicarbonyl compounds.[6] (C) To a methanol solution of sodium hexachlorodipalladate(II), $Na_2[Pd_2Cl_6]$, was added more than twice equivalents of a free ligand followed by an appropriate amount of sodium carbonate.[7] (D) The reaction between [PdCl(hfac)py] and Tl(β-dik) was convenient for preparation of the mixed-ligand palladium(II) chelates containing 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) and another β-diketone.

β-Dicarbonyl compounds were purchased and used without further purification except *t*-butyl acetoacetate which was prepared according to literature.[8] Aqueous solution of $Na_2[PdCl_4]$ was prepared by dissolving palladium(II) chloride and a two and half times molar amount of sodium chloride in a small amount of hot water and adjusting the complex concentration to 0.5 mol dm^{-3}. Methanol solution of $Na_2[Pd_2Cl_6]$ was prepared by dissolving palladium(II) chloride and an equimolar amount of sodium chloride in a small amount of hot methanol and then diluting the resultant solution to [Pd]=0.3 mol dm^{-3}.

Bis(2,4-pentanedionato)palladium(II), $[Pd(acac)_2]$ *(1a)*: An aqueous solution (4 cm^3) of sodium hydroxide (5 mol dm^{-3}) was added with stirring to a mixture of acacH (2.5 cm^3) and a solution (10 cm^3) of $Na_2[PdCl_4]$ (0.5 mol dm^{-3}) to form a yellow precipitate, which was filtered and washed three times each with small portions of water, methanol, and diethyl ether, successively. A yellow powder formed was dissolved in dichloromethane and filtered to avoid a small amount of insoluble material. The solvent was allowed to evaporate spontaneously at room temperature to leave large orange-red crystals (1.37 g) in a 90% yield. The yield is better than that (76%) reported in literature[9] using palladium(II) chloride as a starting material.

cis- *and* trans-*Bis(2,4-hexanedionato)palladium(II),* cis- *and* trans-$[Pd(hxd)_2]$ *(1f)*: The complex was prepared in a similar way as for **1a**. Recrystallization from hot toluene gave orange plates, while a mixture of orange plates and yellow needles was obtained from hot methanol. The yellow needles can conveniently be obtained by prompt evaporation of a dichloromethane solution under reduced pressure. They are geometrical isomers giving identical analyses and slightly different IR and NMR spectra. Orange plates were assigned to *cis* and yellow needles *trans.*

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)palladium(II),$[Pd(hfac)_2]$ *(1d)*: Yellow mercury(II) oxide (6.49 g, 30 mmol) was dissolved in a solution (60 cm^3) of perchloric acid (1 mol dm^{-3}). The solution of mercury(II) perchlorate thus prepared was added with stirring to a solution (20 cm^3) of $Na_2[PdCl_4]$ (0.5 mol dm^{-3}) kept at 0 °C. A greenish yellow precipitate appeared at once but stirring was continued for further several minutes. To the mixture was added dropwise a solution of Na(hfac) which had been prepared by dissolving hfacH (8 cm^3, 50 mmol) in a solution (20 cm^3) of sodium hydroxide (2 mol dm^{-3}). A precipitate was filtered, washed several times with water, and dried *in vacuo*. The red-brown powder was treated with hexane and insoluble material was filtered off. The solvent was distilled away under reduced pressure to leave yellow fine needles (4.71 g) in a 91% yield. Recrystallization from hot hexane gave large red needles, while orange plates of trihydrate were obtained from methanol. When silver(I) nitrate was used instead of mercury(II) perchlorate, the yield was as low as 50%. Compound **1d** must be kept at cold place, since it gradually decomposes at room temperature.

Chloro(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(pyridine)palladium(II), [PdCl(hfac)py]: A solution of **1d** (564 mg, 1.08 mmol) in dichloromethane (2 cm^3) was added to a solution of pyridinium chloride (130 mg, hygroscopic *ca.* 1 mmol) in methanol (5 cm^3) and the mixture was allowed to stand one day at room temperature to deposit red plates (318 mg). Hexane was added to the filtrate and the mixture was cooled to precipitate another crop (53 mg) of the product. The same procedure was repeated once more and the total yield of the product reached 92% (426 mg).

cis- *and* trans-*Bis(1-phenyl-1,3-butanedionato)palladium(II)*, cis- *and* trans-*[Pd(bzac)$_2$]* ***(1g)***: The literature method[10] was improved to attain better yields. A solution (10 cm^3) of potassium hydroxide (1.5 mol dm^{-3}) was added to a solution of bzacH (2.6 g, 16 mmol) in methanol (20 cm^3). A solution (10 cm^3) of $Na_2[PdCl_4]$ (0.5 mol dm^{-3}) was added dropwise through a pipette to the above solution with stirring. A yellow precipitate was filtered, washed three times each with water, methanol, and diethyl ether, and dried *in vacuo*. Compound **1g** was obtained as a mixture of *cis* and *trans* isomers in a 90% yield (1.93 g). When the isomeric mixture was dissolved in dichloromethane and the solvent was evaporated spontaneously at room temperature, only the *trans* isomer was obtained quantitatively as orange-yellow needles. On the other hand, when ethyl acetate (20 cm^3) and petroleum ether boiling below 60 °C (several cm^3) were added to a solution of the *cis-trans* mixture (226 mg) in dichloromethane (25 cm^3) and the solution was kept in a shallow vessel to allow vaporization of solvents at room temperature, both of orange-red hexagonal plates of the *cis* isomer and orange-yellow needles of the *trans* isomer were left to be separated manually. Separation of the isomeric mixture by means of thin layer chromatography was tried over silica gel with dichloromethane as a developing solvent. The R_f values were 0.80 and 0.84 for *cis* and *trans*, respectively. Separation of isomers through a column was not successful because of rather fast isomerization reactions.

Bis(1,1,1-trifluoro-2,4-pentandionato)palladium(II), [Pd(tfac)$_2$] ***(1h)***: To a methanol solution (20 cm^3) of $Na_2[Pd_2Cl_6]$ (0.15 mol dm^{-3}) was added tfacH (1.4 g, 9 mmol) with stirring. On addition of a fine powder of sodium carbonate in limited amounts to the solution, an increasing amount of a yellow precipitate appeared and *ca.* 20 cm^3 of methanol was added to make stirring easy. Addition of the base was stopped when no more precipitate was produced. The precipitate was filtered, washed three times each with water, methanol, and diethyl ether, successively and dried *in vacuo*. Recrystallization from dichloromethane–hexane gave orange-yellow needles (2.0 g) in an 81% yield.

Bis(1,3-diphenyl-1,3-propanedionato)palladium(II), [Pd(dbm)$_2$] ***(1b)***, *bis(2,2,6,6-tetramethyl-3,5-heptanedionato)palladium(II), [Pd(dpm)$_2$]* ***(1c)***, *bis-(3-phenyl-2,4-pentanedionato)palladium(II), [Pd(Ph-acac)$_2$]* ***(1e)***, *bis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)palladium(II), [Pd(pta)$_2$]* ***(1l)***, *and bis(1,1,1-trifluoro-4-(2-thienyl)-2,4-butanedionato)palladium(II), [Pd(tta)$_2$]* ***(1m)***: These complexes were prepared by method C in a similar manner as for **1h**. Recrystallization of **1b**, **1c**, **1e**, and **1l** was performed from dichloromethane–hexane, benzene–hexane, dichloromethane, and diethyl ether, respectively. Compound **1m** is sparingly soluble in common solvents and was not recrystallized.

*Bis(1-*t*-butoxy-1,3-butanedionato)palladium(II), [Pd(buac)$_2$]* ***(1j)***: *t*-Butyl acetoacetate (buacH, 1.5 cm^3, 10 mmol) was dissolved in a solution (10 cm^3) of potassium hydroxide (1 mol dm^{-3}). The solution was added drop by drop with stirring to a solution (10 cm^3) of $Na_2[PdCl_4]$ (0.5 mol dm^{-3}) to deposit a brown precipitate, which was filtered and dried *in vacuo*. The precipitate was dissolved in petroleum ether (bp$<$50 °C, 50 cm^3) and insoluble substance was filtered off. Then the solvent was allowed to evaporate spontaneously at room temperature to deposit light brown plates on the wall of vessel. The yield was 14% (295 mg). *Bis(1-ethoxy-1,3-butanedionato)palladium(II)*,[4] *[Pd(etac)$_2$]* ***(1i)*** and *bis(1-phenyl-3-ethoxy-1,3-propanedionato)palladium(II), [Pd(etbz)$_2$]* ***(1k)*** were also prepared in a similar manner as above.

2,4-Pentanedionato(1,1,1-trifluoro-2,4-pentanedionato)palladium(II), [Pd(acac)(tfac)] ***(1n)***: A methanol solution (20 cm^3) containing K(acac)·H_2O (0.97 g, hygroscopic, *ca.* 6 mmol) and K(tfac)·H_2O (1.35 g, 6.4 mmol) was added with stirring to a methanol solution (20 cm^3) of $Na_2[Pd_2Cl_6]$ (0.15 mol dm^{-3}) to deposit a yellow precipitate. After stirring of the mixture for 2 h, the precipitate was filtered, washed with water and methanol, successively, and dried *in vacuo* to give a yellow powder (1.85 g). Chromatographic separation of the crude product through a silica-gel column (70 × 3d cm) using a mixture of dichloromethane, benzene, and petroleum ether (4 : 1 : 1 by volume) as the developing solvent resulted in three fractions. The middle fraction gave yellow fine needles of **1n** (736 mg) in a 34% yield. The first and third eluents afforded [Pd(tfac)$_2$] (**1h**) and [Pd(acac)$_2$] (**1a**) in each 20% yields, respectively. The same preparative method was applied to various couples of acac, bzac, tfac, and hfac salts, but no mixed-ligand chelate was obtained successfully except the above acac-tfac case.

Alternatively, complex **1n** was also prepared by the partial substitution reaction of [Pd(tfac)$_2$]. To a solution of [Pd(tfac)$_2$] (500 mg, 1.21 mmol) in acetone (20 cm^3) was added with stirring a solution of K(acac)·H_2O (160 mg, *ca.* 1 mmol) in methanol (1 cm^3), when color of the solution changed from yellow to yellow-brown. After stirring of the mixture for 5 min, the solvent was evaporated under reduced pressure to leave a yellow powder, which was extracted with dichloromethane and the extract was subjected to the chromatographic separation as above. Complex **1n** was obtained in a 17% yield (72 mg). The residue which was insoluble in dichloromethane consisted mainly of K(tfac)·H_2O (210 mg, 1.0 mmol).

1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato(2,4-pentanedionato)palladium(II), [Pd(acac)(hfac)] ***(1o)***: A suspension of Tl(acac) (88 mg, 0.29 mmol) in dichloromethane (3 cm^3) was added with stirring to a solution of [PdCl(hfac)py] (152 mg, 0.36 mmol) in dichloromethane (1 cm^3) kept at −10 °C. After stirring of the mixture for 30 min, a white precipitate of thallium chloride was filtered off. Hexane was added to the filtrate and the solution was kept at −20 to −30 °C for 1 h. An additional precipitate of thallium chloride was separated by filtration and the solvent was distilled away under reduced pressure. The residue was dissolved in dichloromethane, hexane was added to the solution, and the mixture was cooled to deposit pale yellow crystals of $[Pd(py)_4](hfac)_2$ accompanied by a powder of thallium chloride. After separation of the precipitate, the solution was poured onto a column of silica gel. Development with dichloromethane gave rise to three zones and the first fraction gave lemon-yellow fine needles of

1o (28 mg) in a 18% yield on the basis of the starting complex. Substances recovered from the second and third fractions were not enough in amount to be identified.

1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato(1-phenyl-1,3-butanedionato)palladium(II), [Pd(bzac)(hfac)] (1p): The same preparative method was used and the first fraction from the column chromatography gave **1p** in a 18% yield. The second fraction contained [Pd(bzac)$_2$] (**1g**) in a 7% yield. The substance in the third fraction was not identified.

Bis(2,4-pentanedionato)platinum(II), [Pt(acac)$_2$] (2a), bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)platinum(II), [Pt(hfac)$_2$] (2d), and cis- *and* trans-*bis(1,1,1-trifluoro-2,4-pentanedionato)platinum(II),* cis- *and* trans-*[Pt(tfac)$_2$] (2h):* These complexes were prepared by the revised method B reported very recently.[6]

2,4-Pentanedionato(1,1,1-trifluoro-2,4-pentanedionato)platinum(II), [Pt(acac)(tfac)] (2n): Both of acacH (5 g, 50 mmol) and tfacH (7.7 g, 50 mmol) were dissolved in a solution (30 cm^3) of sodium hydroxide (5 mol dm^{-3}). To this solution was added with stirring a solution (500 cm^3) of [Pt(H$_2$O)$_4$](ClO$_4$)$_2$[6] (0.025 mol dm^{-3}) followed by a solution (73 cm^3) of sodium hydroxide (5 mol dm^{-3}) drop by drop from pipettes, respectively. A yellow-brown precipitate deposited gradually, which was filtered after being stirred for 15 h, washed three times with water, and dried *in vacuo*. The resultant yellow-brown powder was dissolved in dichloromethane, separated from insoluble material by filtration, and subjected to chromatographic separation through a column of silica gel (70×3d cm) using dichloromethane as the eluent. The first fraction contained [Pt(tfac)$_2$] (**2h**) (656 mg, 10% yield) and the second gave **2n** (1.69 g), which was recrystallized from benzene–hexane to give yellow needles in a 29% yield (1.59 g).

1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato(2,4-pentanedionato)plantinum(II), [Pt(acac)(hfac)] (2o): In a similar manner as above, an equimolar mixture of Na(acac) and Na(hfac) was allowed to react with [Pt(H$_2$O)$_4$](ClO$_4$)$_2$ in aqueous solution and the crude product was subjected to chromatographic separation through a silica-gel column. Development with dichloromethane gave rise to four zones. The first fraction contained [Pt(hfac)$_2$] (547 mg, 7% yield) and the second gave purple fine needles of **2o** in a 15% yield (945 mg). The fourth fraction gave [Pt(acac)$_2$] (1067 mg, 22% yield) and the third a little amount of lemon-yellow substance which was not identified. An analogous preparative trial using a mixture of tfacH and hfacH was not successful in obtaining [Pt(tfac)(hfac)].

Measurements. Infrared spectra were recorded in Nujol on Hitachi 295 and JASCO DS-701G spectrophotometers. JEOL JNM C60HL, MH-100, and FX-60Q instruments were used to obtain NMR spectra. Mass spectra were taken on a JEOL JMS-D300 mass-spectrometer. A vapor-pressure osmometer manufactured by Knauer in West Berlin, West Germany, was also used for molecular-weight determination.

X-Ray Analysis. X-Ray analysis of *cis*-[Pd(bzac)$_2$] (**1g**-*cis*) was performed. Laue symmetry and approximate cell dimensions were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. The cell dimensions were refined by the least-squares analysis of θ values of 16 reflections measured on an automated four-circle diffractometer with Mo $K\alpha$ radiation. Crystal data: Monoclinic, $a=11.024(3)$, $b=19.629(4)$, $c=9.472(2)$ Å, $\beta=119.78(2)^\circ$, space group P2$_1$/c, $D_m=1.60$, $D_c=1.60$ g cm^{-3}, $Z=4$, μ(Mo $K\alpha$)=10.5 cm^{-1}.

Intensity data were collected by the ω-2θ scan method by the diffractometer with graphite-monochromated Mo $K\alpha$ radiation, using a crystal specimen with size of 0.22×0.30×0.08 mm^3. The scan speed and scan width in ω were 0.017 s^{-1} and $(0.7+0.2 \tan\theta)^\circ$, respectively. The background was counted for 20 s at each side of the scan range. A total of 1927 unique reflections having intensity $I_t-2\sqrt{I_t}>I_b$ was collected in the $2\theta\leq55^\circ$ range (I_t, intensity at the peak of reflection; I_b, mean background intensity obtained from preliminary background measurement of 5 s at each side of the scan range). The intensities of three standard reflections monitored every 4 h showed no appreciable variation. Intensities were corrected for Lp factor but not for absorption. Of 1927 reflections 1814 with $F_o^2>3\sigma(F_o^2)$ were used for the structure analysis.

The crystal structure was solved by the heavy atom method, and the positional and thermal parameters were refined by the least-squares. The minimized function was $\sum w(F_o-|F_c|)^2$. The weighting scheme, $w=0.82$ for $F_o<35.7$, $w=1.0$ for $35.7\leq F_o\leq71.4$, and $w=(71.4/F_o)^2$ for $F_o>71.4$, were found to be optimal. All H atoms could be located on the difference Fourier map calculated after anisotropic refinement for nonhydrogen atoms. These H atoms were included in the least-squares refinement with isotropic temperature factor $B_H=B_p+1.0$ Å^2, the positional parameter being fixed (B_p, the isotropic temperature factor of nonhydrogen atom to which the H atom is bonded). The convergence was attained with $R=0.033$ and $R'(=[\sum w(F_o-|F_c|)^2/\sum wF_o^2]^{1/2})=0.042$.

TABLE 1. FINAL ATOMIC PARAMETERS(×10^4)

	x	y	z	$B^{a)}$/Å^2
Pd	344.9(5)	1037.8(2)	927.6(5)	2.43(1)
O(1)	1476(4)	1564(2)	222(5)	2.9(1)
O(2)	−1213(4)	1702(2)	35(4)	2.6(1)
O(3)	1948(4)	406(2)	1883(5)	2.9(1)
O(4)	−802(4)	490(2)	1573(5)	2.6(1)
C(1)	1937(7)	2310(3)	−1348(9)	3.6(2)
C(2)	977(6)	2056(3)	−780(7)	2.8(2)
C(3)	−303(6)	2366(3)	−1310(7)	2.8(2)
C(4)	−1285(6)	2214(3)	−858(6)	2.6(1)
C(5)	−2555(6)	2653(3)	−1367(7)	2.8(2)
C(6)	−2643(7)	3306(3)	−1991(9)	3.6(2)
C(7)	−3829(8)	3694(4)	−2419(10)	4.4(2)
C(8)	−4917(8)	3449(4)	−2278(10)	4.7(2)
C(9)	−4803(8)	2808(5)	−1646(11)	5.1(3)
C(10)	−3630(7)	2409(4)	−1171(10)	4.1(2)
C(11)	3249(7)	−567(4)	3145(9)	4.1(2)
C(12)	1951(6)	−157(3)	2543(7)	2.9(2)
C(13)	865(6)	−404(3)	2760(7)	2.7(2)
C(14)	−413(6)	−89(3)	2285(6)	2.5(2)
C(15)	−1462(6)	−422(3)	2623(7)	2.6(2)
C(16)	−2867(7)	−411(4)	1477(8)	3.4(2)
C(17)	−3831(7)	−700(4)	1817(10)	4.2(2)
C(18)	−3401(8)	−1013(4)	3291(9)	3.8(2)
C(19)	−2017(7)	−1036(4)	4429(8)	3.7(2)
C(20)	−1034(7)	−756(3)	4088(7)	3.1(2)

a) Equivalent isotropic temperature factor.

Atomic scattering factors were taken from Ref. 11. Real part of the anomalous dispersion corrections were applied for Pd^0. Atomic coordinates are given in Table 1. The anisotropic thermal parameters, H atom coordinates, and F_o-F_c tables are preserved by the Chemical Society of Japan (Document No. 8127). All computations were performed on a FACOM 230-60 computer at the Osaka City University using programs in the UNICS.[12]

Results and Discussion

Syntheses. A number of palladium(II) (**1**) and platinum(II) (**2**) bis-chelates of β-dicarbonyl compounds were prepared including the binary chelates of both the symmetric (**1a**—**1e**, **2a**, and **2d**) and unsymmetric (**1f**—**1m** and **2h**) β-dicarbonyl anions as well as the mixed-ligand chelates (**1n**—**1p**, **2n**, and **2o**). The appearance, preparative method, yield, decomposition temperature, and elemental analyses of the new compounds are listed in Table 2 together with some molecular-weight data.

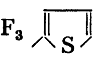
Of the four preparative methods summarized at the outset, method A represented by Eq. 1 is suitable for

$$[MCl_4]^{2-} + 2(\beta\text{-dik})^- \longrightarrow [M(\beta\text{-dik})_2] + 4Cl^- \qquad (1)$$

more basic anions such as those of acacH, bzacH, and the β-keto esters. Very low yields of the β-keto-ester chelates may be related to weaker basicity of the oxygen atoms than that of the central carbon atom in the ligand anions as exemplified by the low [enol]/[keto] values of the β-keto ester molecules.[13] The fact that both of the chelating ligands in [Pd(etac)$_2$] (**1i**) are readily transformed to the central-carbon-bonded state on reactions with nitrogen bases,[4] whereas only one of the acac anions in [Pd(acac)$_2$] (**1a**) is converted in similar reactions[14] also shows the difference in the preference of bonding modes between acac and β-keto ester anions.

In the platinum(II) case, method A affords [Pt(acac)$_2$] (**2a**) in a much lower yield (35%) than that for [Pd(acac)$_2$] together with the central-carbon-bonded by-products such as K[PtCl(acac)(acac-*C*^{3})] and K[PtCl$_2$(acac-*C*^{3})$_2$].[15] Furthermore the platinum(II) chelates of less basic tfac and hfac anions have not been obtained. The Pt–Cl bonds might be more stable than the Pt–(β-dik) chelate, resisting the ligand substitution. On this supposition, the chloride anions in [MCl$_4$]$^{2-}$ were displaced by virtue of mercury(II)[16] and/or silver(I) ions prior to reactions with the β-dik ligands.[6] Thus

TABLE 2. NEWLY PREPARED M(R^{1}COCXCOR^2)$_2$ COMPLEXES OF PALLADIUM(II) (**1**) AND PLATINUM(II) (**2**)[a)]

No.	Complex R^1 R^2	Appearance (Prep. method[b)])	Yield %	Dec temp °C	Found (Calcd) C %	H %	Mol wt
1d[c)]	[Pd(hfac)$_2$]	Yellow needles	91	46—55[d)]	23.19	0.43	520[e)]
	CF_3 CF_3	(B)			(23.07)	(0.39)	(520.5)
1e[f)]	[Pd(Ph-acac)$_2$]	Yellow plates	96	230—235	57.89	4.80	
	CH_3 CH_3	(C)			(57.84)	(4.85)	
1f-*cis*	[Pd(hxd)$_2$]	Orange plates		120—121[d)]	43.42	5.50	332[e)]
	CH_3 C_2H_5	(A)			(43.32)	(5.45)	(332.7)
1f-*trans*		Yellow needles	90	114—115[d)]	43.37	5.45	
1g-*cis*	[Pd(bzac)$_2$]	Orange-red	≈40	240—242	55.79	4.22	
	CH_3 C_6H_5	plates (A)			(56.02)	(4.23)	
1g-*trans*		Orange-yellow needles	90	238—240	55.67	4.22	
1h	[Pd(tfac)$_2$]	Orange-yellow	81	≈200	29.12	1.96	412[e)]
	CH_3 CF_3	needles (C)			(29.11)	(1.95)	(412.6)
1j	[Pd(buac)$_2$]	Light brown	14	≈103	45.25	6.33	407[g)]
	CH_3 $OC_4H_9{}^t$	plates (A)			(45.67)	(6.23)	(420.8)
1k	[Pd(etbz)$_2$]	Orange cryst	≈3	145—150	53.87	4.54	531[g)]
	C_6H_5 OC_2H_5	(A)			(54.05)	(4.54)	(488.8)
1l	[Pd(pta)$_2$]	Orange-yellow	95	≈100[d)]	38.23	4.01	496[e)]
	CF_3 $C_4H_9{}^t$	needles (C)			(38.69)	(4.06)	(496.7)
1m	[Pd(tta)$_2$]	Yellow powder	95	235—236	34.87	1.44	
	CF_3 	(C)			(35.02)	(1.47)	
1n	[Pd(acac)(tfac)]	Yellow fine	34	90—92[d)]	33.67	3.15	358[e)]
		needles (C)			(33.49)	(3.09)	(358.6)
1o	[Pd(acac)(hfac)]	Yellow fine	18	80—82[d)]	29.06	1.97	412[e)]
		needles (D)			(29.11)	(1.95)	(412.6)
1p	[Pd(bzac)(hfac)]	Yellow needles	18	119—121[d)]	38.04	2.16	474[e)]
		(D)			(37.96)	(2.12)	(474.6)
2n	[Pt(acac)(tfac)]	Yellow needles	29	≈114[d)]	26.76	2.43	447[e)]
		(B)			(26.85)	(2.48)	(447.3)
2o	[Pt(acac)(hfac)]	Purple fine	15	≈78[d)]	23.76	1.49	501[e)]
		needles (B)			(23.96)	(1.61)	(501.2)

a) X=H except compound **1e** for which X=C_6H_5. b) See text. c) Trihydrate, orange crystals. Found: C, 20.99; H, 1.11%. Calcd: C, 20.90; H, 1.40%. d) Sublimation temperature. e) Parent peaks in mass spectra containing the ^{106}Pd or ^{195}Pt atom were used. f) The ligand is 3-phenyl-2,4-pentanedionate. g) Determined by the vapor pressure osmometry in chloroform at 42 °C.

the chelate formation reactions in method B are expressed by Eq. 2. $[Pd(tfac)_2]$ (**1h**) was prepared in a high yield by the reaction between $Na_2[Pd_2Cl_6]$ and tfacH in cooperation with sodium carbonate. Method C7) is convenient and successfully applied to preparation of the $[Pd(\beta\text{-dik})_2]$ complexes other than **1d**.

$$[M(H_2O)_4]^{2+} + 2(\beta\text{-dik})^- \longrightarrow [M(\beta\text{-dik})_2] + 4H_2O. \quad (2)$$

$$[Pd_2Cl_6]^{2-} + 4(\beta\text{-dik})^- \xrightarrow[\text{in MeOH}]{} 2[Pd(\beta\text{-dik})_2] + 6Cl^- \quad (3)$$

By employing an equimolar mixture of two kinds of β-dicarbonyl compounds, [Pd(acac)(tfac)] (**1n**), [Pt(acac)(tfac)] (**2n**), and [Pt(acac)(hfac)] (**2o**) were obtained according to methods C, B, and B, respectively. In each of these cases binary bis-chelates were accompanied and separated by column chromatography. On the other hand, [Pd(acac)(hfac)] (**1o**) and [Pd(bzac)(hfac)] (**1p**) could not be prepared by this way, but were obtained by the metal-assisted ligand substitution reactions of [PdCl(hfac)(py)] with Tl(β-dik) (method D). Unfortunately the yield was low in either case and the desired reaction 4 seems to be accompanied by subsidiary reactions 5 and 6. The by-product $[Pd(py)_4](hfac)_2$ was identified by comparison with the authentic sample prepared by the reaction between $[Pd(hfac)_2]$ and pyridine.17)

$$[PdCl(hfac)(py)] + Tl(\beta\text{-dik}) \longrightarrow [Pd(hfac)(\beta\text{-dik})] + py + TlCl \quad (4)$$

$$[Pd(hfac)(\beta\text{-dik})] + Tl(\beta\text{-dik}) \longrightarrow [Pd(\beta\text{-dik})_2] + Tl(hfac) \quad (5)$$

$$[PdCl(hfac)(py)] + Tl(hfac) + 3py \longrightarrow [Pd(py)_4](hfac)_2 + TlCl \quad (6)$$

Geometrical isomerism is possible in the case of $[M(\beta\text{-dik})_2]$ complexes containing unsymmetrical β-dicarbonyl compounds as a ligand. The structures of *cis*-$[VO(bzac)_2]$,18) *cis*-$[Zn(bzac)_2]\cdot EtOH$,19) *trans*-$[Cu(bzac)_2]$,20) *trans*-$[Pd(bzac)_2]$,10) and *trans*-$[Cu(etac)_2]$21) were confirmed by X-ray analysis, but their geometrical isomers have not been reported and identification of isomers in solution has not been performed either, except for $[Pd(etac)_2]$.4) Recrystallization of $[Pd(bzac)_2]$ (**1g**) from dichloromethane gave only orange-yellow needles of the *trans* isomer which had been reported.10)

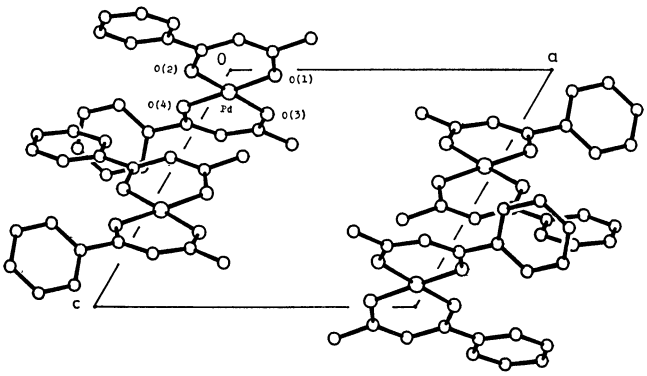


Fig. 1. The crystal structure of *cis*-$[Pd(bzac)_2]$ viewed down the b axis.

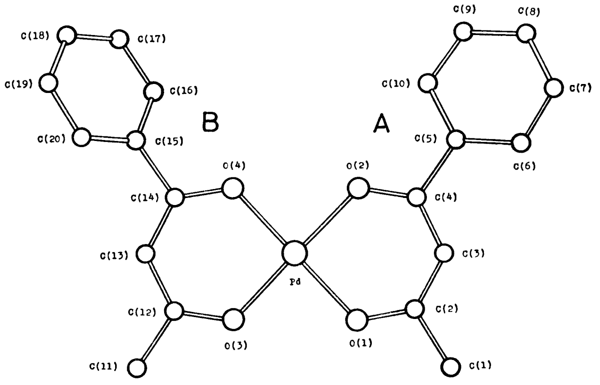


Fig. 2. The molecular structure of *cis*-$[Pd(bzac)_2]$ viewed normal to the coordination plane.

Table 3. Bond lengths and angles

Bond lengths (l/Å)			
Pd–O(1)	1.974(5)	Pd–O(3)	1.973(5)
Pd–O(2)	1.980(4)	Pd–O(4)	1.974(5)
O(1)–C(2)	1.271(8)	O(3)–C(12)	1.270(8)
O(2)–C(4)	1.289(8)	O(4)–C(14)	1.282(8)
C(1)–C(2)	1.492(11)	C(11)–C(12)	1.487(11)
C(2)–C(3)	1.382(10)	C(12)–C(13)	1.398(9)
C(3)–C(4)	1.380(10)	C(13)–C(14)	1.392(9)
C(4)–C(5)	1.505(9)	C(14)–C(15)	1.495(9)
Bond angles (ϕ/°)			
O(1)–Pd–O(2)	94.0(2)	O(3)–Pd–O(4)	94.7(2)
Pd–O(1)–C(2)	122.5(4)	Pd–O(3)–C(12)	123.7(4)
Pd–O(2)–C(4)	123.4(4)	Pd–O(4)–C(14)	123.2(4)
O(1)–C(2)–C(3)	126.2(6)	O(3)–C(12)–C(13)	125.6(6)
C(2)–C(3)–C(4)	127.5(7)	C(12)–C(13)–C(14)	126.9(6)
C(3)–C(4)–O(2)	124.7(6)	C(13)–C(14)–O(4)	125.8(6)
O(1)–C(2)–C(1)	113.7(6)	O(3)–C(12)–C(11)	115.2(6)
C(1)–C(2)–C(3)	120.1(6)	C(11)–C(12)–C(13)	119.2(6)
O(2)–C(4)–C(5)	113.7(6)	O(4)–C(14)–C(15)	114.0(6)
C(3)–C(4)–C(5)	121.6(6)	C(13)–C(14)–C(15)	120.2(6)

TABLE 4. DEVIATIONS OF ATOMS FROM MEAN PLANES AND INTERPLANAR ANGLES

Deviations (d) of atoms from planes[a)]

Plane	Deviation (d/Å)
(1)	O(1)* 0.035, O(2)* −0.035, O(3)* −0.034, O(4)* 0.036, Pd 0.004, C(1) 0.464, C(2) 0.272, C(3) 0.321, C(4) 0.115, C(5) 0.024, C(11) 0.029, C(12) 0.034, C(13) 0.087, C(14) 0.092, C(15) 0.140
(2)	O(1)* −0.020, O(2)* 0.031, C(2)* 0.018, C(3)* 0.014, C(4)* −0.041, Pd 0.233, C(1) 0.021, C(5) −0.217
(3)	O(3)* −0.001, O(4)* −0.000, C(12)* 0.003, C(13)* −0.003, C(14)* 0.002, Pd 0.065, C(11) −0.012, C(15) −0.018
(4)	C(5)* 0.010, C(6)* 0.003, C(7)* −0.013, C(8)* 0.009, C(9)* 0.003, C(10)* −0.011
(5)	C(15)* −0.017, C(16)* 0.007, C(17)* 0.003, C(18)* −0.003, C(19)* −0.010, C(20)* 0.019

a) Atoms marked with an asterisk were included in the calculation of the mean plane.

Interplanar angles (ϕ/°)

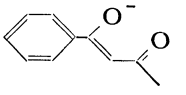
(1)—(2)	170.1
(1)—(3)	177.0
(2)—(4)	17.0
(3)—(5)	41.1

On the other hand, orange-red hexagonal plates of the *cis* isomer accompanied by *trans* appeared from a mixture of dichloromethane, ethyl acetate, and petroleum ether. Detail of the X-ray structure of *cis*-[Pd(bzac)$_2$] is reported below. The isomeric pairs of [Pt(tfac)$_2$][6)] and [Pd(hxd)$_2$] were also isolated and characterized. Isomers of the other [Pd(β-dik)$_2$] complexes of unsymmetric ligands were not isolated but were identified in solution by ^{1}H NMR spectroscopy as will be described in later sections.

X-Ray Structure of cis-*[Pd(bzac)$_2$].* Figures 1 and 2 show the crystal structure and a view of the molecule normal to the coordination plane defined by four oxygen atoms. Bond lengths and angles are given in Table 3. Table 4 lists deviations of atoms from least-squares plane. The Pd atom has a usual square-planar coordination by four oxygen atoms. Both O–C–C–C–O planes in the six-membered chelate rings are slightly bent upward from the coordination plane, the interplanar angles being given in Table 4. The C(13) atom of the adjacent molecule ($-x$, $-y$, $-z$), the mean molecular plane of which is parallel to that of the molecule (x, y, z) under consideration, is located just above the Pd atom. The Pd···C(13) distance is 3.301(7) Å, and Pd···C(13) vector intersects the coordination plane at 80.8°.

The phenyl group is rotated about C–C bond joining the group to the chelate ring, being slant against the O–C–C–C–O plane. The torsion angle is 17.0° in the ligand A and 41.1° in B.[22)] In the other metal chelates of the bzac the torsion angles are in the 4—23° range (6.5° and 19.0° in *cis*-[VO(bzac)$_2$],[18)] 14.3° in *trans*-[Cu(bzac)$_2$],[20)] 23° in *trans*-[Pd(bzac)$_2$],[10)] 3.8° and 7.5° in *cis*-[Zn(bzac)$_2$]·EtOH.[19)]). The ligand conformation for A is therefore thought to be preferred over that for B with larger torsion angle. The unfavorable conformation of B presumably results from crystal packing.

The approximate coplanarity of the phenyl and chelate rings in the preferred conformation suggests a conjugation of π systems between two rings. On the basis of the X-ray structures of the *trans* isomers of Cu and Pd complexes, Hon *et al.*[10)] claimed that there is an effective inter-ring conjugation and that the chelate ring has a significant contribution from the following resonance structure. In the case of the *cis* isomer of Pd



complex, however, the bond lengths in the O–C–C–C–O segment of A show no localization of π electrons. The C(4)–C(5) bond length, which may reflect the extent of the conjugation, is not different from the length for single C(sp^2)–C(sp^2) bond. Furthermore the structural parameters in A agree well with chemically equivalent ones in B of which larger torsion angle indicates smaller inter-ring conjugation; the extent of conjugation is not detectable from structural parameters. Bond lengths and angles in the chelate rings of *cis*-[Pd(bzac)$_2$] are rather in agreement with the corresponding ones in Pd(acac)$_2$(TTF)[23)] (TTF=tetrathiafulvalene).

Thermal Stability and IR Spectra. Most of the chelates in Table 2 are thermally stable and the following features in volatility are noted which are similar to those observed for the β-dicarbonyl chelates of other metals.[2)] (i) When the methyl groups in acac are replaced by the ethyl, *t*-butyl, and trifluoromethyl groups, volatility of the complex increases in this sequence. (ii) Substitution with phenyl and thienyl groups makes the complex less volatile. (iii) Sublimation temperature of a mixed-ligand chelate is intermediary of those for the two binary chelates. As is indicated in Table 2, molecular-weight data of volatile complexes were determined by mass spectrometry.

Infrared bands in the 1650—1500 and 830—770 cm^{-1} regions which are assigned to the ν(C⩵O)+ν(C⩵C) and chelate-ring π(CH) vibrations, respectively,[24)] are listed in Table 5 together with some other characteristic vibrations. Substitution of the methyl group in the acac chelate with the electron-attracting trifluoromethyl group increases the ν(C⩵O)+ν(C⩵C) frequencies. IR spectra in the higher frequency region are not so sensitive to the geometry of complexes, but those in the region lower than 700 cm^{-1} show ap-

TABLE 5. CHARACTERISTIC IR BANDS (cm^{-1}) IN NUJOL

No.	ν(C$\cdots$O)+ν(C$\cdots$C)	π(CH)	Other bands
1a[a)]	1563vs, 1545vs, 1524vs	787s, 780s	
1b	1585m, 1530vs, 1520vs		
1c[b)]	1589m, 1530vs, 1498vs	796s	
1d	1591vs, 1552m, 1529m	810vs	ν(C–F): 1260vs, 1210vs, br, 1145—1170vs, br
1e	1560—1540vs	774s	
1f-*cis*	1545vs, 1518vs	820s, 793s	
1f-*trans*	1560vs, br 1520vs	803m, 780s	
1g-*cis*	1582m, 1540—1510vs, br	785s	
1g-*trans*[c)]	1584m, 1540—1510vs, br	772s	
1h-*trans*	1595vs, 1579vs, 1517s	799s	ν(C–F): 1228vs, 1183vs, 1155vs, 1038vs
1i[d)]	1587vs, 1552s, 1515vs	785s	ν(C–O): 1181vs
1j	1582vs, 1560vs, 1510vs	800s	ν(C–O): 1178vs
1k	1590vs, 1560vs, 1515vs	777vs	ν(C–O): 1210vs
1*l*	1612m, 1581vs, 1536m, 1512s	807s	
1m	1585s, sh, 1560vs, br, 1530s, 1505m	794s, 785m	
1n	1605vs, 1568vs, 1519vs	799m, 790s, 780m	ν(C–F): 1230vs, 1190vs, br, 1145vs, br
1o	1620vs, 1597m, 1551vs, 1520vs	802s, 796s	ν(C–F): 1266vs, 1210vs, br, 1150vs
1p	1626vs, 1605vs, 1589vs, 1548vs, 1530vs, 1515vs		
2a[e)]	1560vs, 1550vs, 1528vs	775vs	
2d[f)]	1585vs, 1557w, 1533w	816s	ν(C–F): 1265vs, 1210vs, 1155vs
2h-*cis*[f)]	1590vs, br, 1530vs	807vs	ν(C–F): 1235s, 1192vs, 1140vs, br
2h-*trans*[f)]	1580vs, br, 1517vs	804vs	ν(C–F): 1190vs, 1160vs, br, 1140vs
2n	1601m, 1564s, 1525vs	798m, 790s, 780m,	ν(C–F): 1232s, 1188s, br, 1150vs
2o	1589s, 1550vs, 1529vs	802s	ν(C–F): 1275vs, 1262vs, 1201vs, 1154vs

a) Mikami, *et al.* recorded the corresponding bands at 1569, 1549, 1524, 786, and 779 cm^{-1} [M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, **23**, 1037 (1967)]. b) The spectrum was shown in Ref. 7. c) Nakamoto, *et al.* recorded only the ν(Pd–O) band at 478 cm^{-1} for [Pd(bzac)$_2$] [K. Nakamoto, P. J. McCarthy, and A. E. Martell, *Nature*, **183**, 459 (1959)]. As is seen in Fig. 3, this band may be assigned to the *trans* isomer. d) Exact frequencies were not given in Ref. 4. e) The corresponding literature data probably in KBr are 1565s, 1555s, 1527s, and 774s cm^{-1} [J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, **1965**, 6740]. f) Ref. 6.

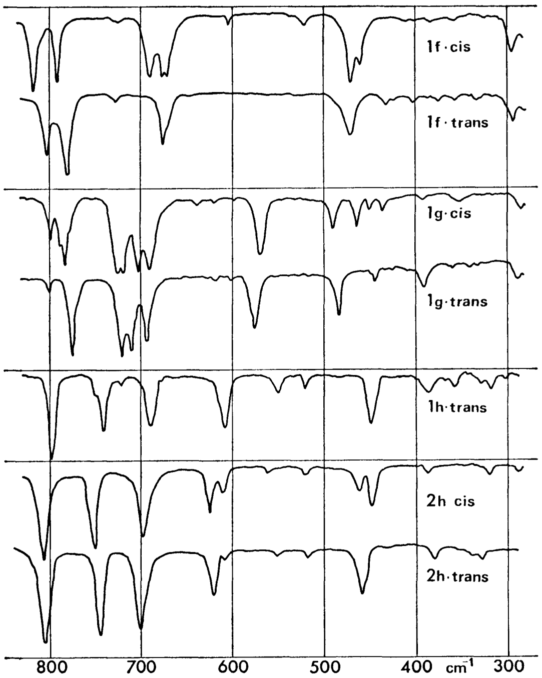


Fig. 3. IR spectra in Nujol in the lower-frequency region of [Pd(hxd)$_2$] (**1f**), [Pd(bzac)$_2$] (**1g**), [Pd(tfac)$_2$] (**1h**), and [Pt(tfac)$_2$] (**2h**).

preciable difference between the *cis* and *trans* isomers. Figure 3 compares the spectra of three isomeric pairs. In accordance with the lower symmetry, *cis* isomers of [Pd(hxd)$_2$] (**1f**), [Pd(bzac)$_2$] (**1g**) and [Pt(tfac)$_2$] (**2h**) exhibit more composite spectra than *trans* isomers. The spectrum of [Pd(tfac)$_2$] (**1h**) in this region shows a close resemblance to that of *trans*-**2h** and may be considered to be *trans*, although the *cis* isomer has not yet been isolated. As is seen in Fig. 3, orange plates of [Pd(hxd)$_2$] (**1f**) show more composite IR spectra than yellow needles and are tentatively assigned to the *cis* isomer.

IR spectrum of a mixed-ligand chelate [M(β-dik)(β-dik')] looks like a superposition of spectra of the binary chelates [M(β-dik)$_2$] and [M(β-dik')$_2$] and is complicated especially in the π(CH) and lower-frequency regions.

NMR Spectra. Tables 6—10 list the ^{1}H, ^{13}C, and ^{19}F NMR data. Substitution of the CH$_3$ group with CF$_3$ deshields the methine proton but increases shielding of the methine carbon. Inductive effect of the CF$_3$ group might shift the shared electrons of the C–H bond to the carbon side. It is noticed that C$_6$D$_6$ shows a remarkable effect on the ^{1}H NMR spectra, most signals showing substantial upfield shifts as compared with those taken in other solvents. Strange to say, the methyl protons of [M(acac)$_2$] (**1a** and **2a**)

TABLE 6. ^{1}H NMR DATA FOR THE BINARY [$M(R^1COCXCOR^2)_2$] COMPLEXES OF PALLADIUM(II) (**1**) AND PLATINUM(II) (**2**)[a)]

No.	Solvent	δ[J(Pt-H)] CH_3	δ[J(Pt-H)] CH	δ(J(H-H)) Other	[*cis*]/[*trans*]
1a	$CDCl_3$	2.07	5.43		
	C_6D_6	1.65	4.94		
	$(CD_3)_2CO$	1.97	5.49		
	$(CD_3)_2SO$	1.97	5.53		
1b	$CDCl_3$		6.77	C_6H_5: 7.5m, 8.0m	
1c	$CDCl_3$[b)]		5.67	$C(CH_3)_3$: 1.14	
	C_6D_6		5.74	$C(CH_3)_3$: 1.13	
1d	$CDCl_3$		6.42		
	C_6D_6		5.92		
	CD_3OD		6.50		
	$(CD_3)_2CO$		6.60		
1e	$CDCl_3$	1.83		C_6H_5: 7.2m	
	C_6D_6	1.67		C_6H_5: 6.7m, 7.0m	
1f[c)]	$CDCl_3$	2.08	5.43	CH_2-CH_3: $\left.\begin{matrix}2.36q\\2.34q\end{matrix}\right\}$ −1.12t(7)	1/1[d)]
	C_6D_6	1.71	5.08	CH_2-CH_3: $\left.\begin{matrix}2.23q\\2.05q\end{matrix}\right\}$ −0.98t(7)	1/1[d)]
1g-*cis*	$CDCl_3$	2.20	6.06	C_6H_5: 7.4m, 7.9m	2/1
1g-*trans*	$CDCl_3$	2.20	6.04	C_6H_5: 7.4m, 7.9m	
1h	$CDCl_3$	2.26	5.92		
	C_6D_6	$\left.\begin{matrix}1.36\\1.32\end{matrix}\right\}$	5.35		1/3
1i	$CDCl_3$	$\left.\begin{matrix}1.93\\1.98\end{matrix}\right\}$	4.78	CH_2-CH_3: $\left.\begin{matrix}4.12q\\4.19q\end{matrix}\right\}$ −1.25t(7)	3/7
	C_6D_6	1.71	4.85	CH_2-CH_3: 3.88q− $\left\{\begin{matrix}0.84t\\0.91t\end{matrix}\right.$(7)	1/1
1j	$CDCl_3$	1.92	4.63	$C(CH_3)_3$: 1.40	e)
1k[c)]	$CDCl_3$		5.43	C_6H_5: 7.3m, 7.7m CH_2-CH_3: 4.18q−1.29t(7) 4.27q−1.32t(7)	1/1
1l[c)]	$CDCl_3$		6.01	$C(CH_3)_3$: 1.17	
	C_6D_6		5.87	$C(CH_3)_3$: 0.83, 0.78	6/5 or 5/6
2a	$CDCl_3$[f)]	1.95[4.9]	5.54[10.7]		
	C_6D_6	1.49[4.9]	4.98[10.5]		
2d[g)]	$CDCl_3$		6.50[10.5]		
2h-*cis*	$CDCl_3$[g)]	2.08[3.9]	6.01[10.5]		
	C_6D_6	1.17[4]	5.54[10]		
2h-*trans*	$CDCl_3$[g)]	2.09[4]	6.01[11]		
	C_6D_6	1.10[4]	5.40[10]		

a) X=H except **1e** for which $X=C_6H_5$. When two values of chemical shift are given for a signal from a mixture of geometric isomers, the former one refers to *cis* and the latter to *trans*. Chemical shifts are given in ppm from internal Me_4Si and J values in Hz. m, multiplet; q, quartet; t, triplet; others, singlet. b) The literature values are CH: 5.65 and $C(CH_3)_3$: 1.13 ppm.[7)] c) Identification of isomers is not possible. d) The isomer ratio was determined based on the ^{13}C NMR spectra. e) Only one isomer seems to exist, but is not identified. f) The literature values are CH_3: 2.08[5] and CH: 5.53[11] [J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, **1965**, 6740]. g) Redetermined[6)] on an FX-60Q instrument.

resonate at higher field in $CDCl_3$ but at lower field in C_6D_6 than those of [$M(tfac)_2$] (**1h** and **2h**), respectively. Similar reversion of the methyl-signal positions in the two solvents was also observed for similar Zr(IV), Hf(IV), Ce(IV), and Th(IV) complexes, and even for free ligands, acacH and tfacH.[25)] The upfield shift in benzene may be attributed to the diamagnetic anisotropy of the solvent molecule interacting with the chelates and ligands, but reasonable rationalization of much more remarkable effect exerted on the tfac chelates than on the acac chelates is not possible at present.

NMR spectra are useful for distinguishing between geometrical isomers of bis-chelates of unsymmetrical ligands. The platinum(II) chelates are very inert and both isomers of [$Pt(tfac)_2$] (**2h**) showed no sign of isomerization in C_6D_6 for more than one month. The corresponding palladium(II) complex [$Pd(tfac)_2$] (**1h**) showed a single methyl signal at 1.32 ppm immediately after dissolution in C_6D_6, but a new signal at 1.36 ppm grew gradually with time at the expense of the 1.32 ppm signal to attain equilibrium within one day at the area ratio of 3 : 1. By reference to the spectra of **2h**

Table 7. ^{1}H NMR data for the mixed-ligand chelates [M(β-dik)(β-dik′)] of palladium(II) (**1**) and platinum(II) (**2**)[a]

No.	Solvent	β-dik	δ [J(Pt–H)] CH_3	 CH	 Other
1n	$CDCl_3$	acac	2.08	5.44	
		tfac	2.19	5.83	
	C_6D_6	acac	1.59, 1.55	4.80	
		tfac	1.38	5.35	
1o	$CDCl_3$	acac	2.13	5.51	
		hfac		6.22	
1p	$CDCl_3$	bzac	2.26	6.15	C_6H_5: 7.5m, 7.8m
		hfac		6.25	
2n	$CDCl_3$	acac	1.99[≈5]	5.58[11.5]	
		tfac	2.03	5.96[9.8]	
	C_6D_6	acac	1.46[5], 1.41[5]	4.91[12]	
		tfac	1.15[4]	5.42[10]	
2o	$CDCl_3$	acac	2.02[5.6]	5.63[12.2]	
		hfac		6.30[9.0]	
	C_6D_6	acac	1.41[5.9]	4.89[12.2]	
		hfac		5.91[8.8]	

a) Chemical shifts in ppm from internal Me_4Si and J(Pt–H) values in brackets in Hz.

Table 8. $^{13}C\{^1H\}$ FT NMR data in $CDCl_3$ for the binary chelates[a]

No.	δ [J(Pt–C)] (J(F–C)) CH_3	 CF_3	 CH	 $CH_3\underline{C}O$	 $CF_3\underline{C}O$	 Other[b]
1a[c]	25.4		101.6	187.2		
1a[d]	24.9		101.1	186.8		
1a[e]	25.0		101.4	j)		
1b			95.8	181.6		Ph: C^1, 136.6; C^2, 128.4; C^3, 127.6; C^4, 131.4
1c			91.8	196.2		*t*-Bu: C^1, 40.5; C^2, 28.6
1d		114.7q (284)	93.8m (1.6)		176.2q (37)	
1d[d]		115.1q (284)	93.6br		175.5q (37)	
1d[e]		115.8q (283)	94.9m (1.8)		176.5q (37)	
1e	26.9			186.1		Ph: C^1, 140.3; C^2, 128.9; C^3, 131.5; C^4, 127.2
1f-*cis*	25.5_0		99.9_3	191.2_4		$\underline{C}O\underline{C}H_2\underline{C}H_3$: 187.2_2, 32.2_5, 11.4_5
1f-*trans*	25.4_8		99.9_1	191.3_1		187.0_3, 32.2_2, 11.2_8
1f-*cis*[d]	25.0_0		99.9_1	190.9_1		$\left.\begin{matrix}187.0_6\\187.0_3\end{matrix}\right\}$ 32.2_3, 11.3_3
1f-*trans*[d]	24.9_6		99.8_9	190.9_0		
1g-*cis*[f]	28.2_1		98.4_0	188.3_7		PhCO: C^1, 135.8_0; C^2, 127.4_2; C^3, 121.1_8; C^4, 131.3_2; CO, 179.9_9
1g-*trans*[f]	28.1_6		98.5_7	188.6_6		PhCO: C^1, 135.9_7; C^2, 127.4_2; C^3, 121.1_8; C^4, 131.2_2; CO, 179.9_9
1h	26.8	j)	97.8	195.4	j)	
1i[g]	24.6		86.3	187.1		CO_2Et: CO, 171.3(*cis*), 171.1(*trans*); CH_2, 61.8(*cis*), 61.6(*trans*); CH_3, 14.3.
1i[d]	$\left.\begin{matrix}24.5\\24.4\end{matrix}\right\}$		$\left.\begin{matrix}86.4\\86.2\end{matrix}\right\}$	$\left.\begin{matrix}187.6\\187.9\end{matrix}\right\}$		CO_2Et: CO, 171.5, 171.9; CH_2, 61.9, 61.4; CH_3, 14.2
2a[h]	25.5 [43]		102.9 [74]	185.3 [25]		
2d		115.1q [67](283)	96.0 [77]		173.5q [24](37)	
2h-*cis*[i]	26.9 [45]	116.1q [67](283)	99.4 [76](≈2)	192.8 [26]	166.5q [≈23](34)	
2h-*trans*[i]	27.0 [46]	116.2q [j](281)	99.4 [74]	193.5 [24]	j)	

a) Chemical shifts in ppm from internal Me_4Si and J(Pt–C) in brackets and J(F–C) in parentheses in Hz. b) Numbering of the phenyl-ring carbons: quaternary, C^1; ortho, C^2; meta, C^3; para, C^4. Signal assignments to C^2 and C^3 might be inverted. Numbering of the *t*-butyl carbons: quaternary, C^1; primary, C^2. c) Similar data were recorded in literatures: T. Ito, T. Kiriyama, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3250 (1976); Y. Senda, A. Kasahara, A. Suzuki, *ibid.*, **49**, 3337 (1976). d) In C_6D_6. e) In $(CD_3)_2CO$. f) The major component in equilibrium was assigned to *cis*. g) The major component in $CDCl_3$ was assigned to *trans*, but the equi-intensity couples of signals in C_6D_6 can not be distinguished. h) Similar data for **2a** as well as for **1a** were reported by C. A. Wilkie and D. T. Haworth, *J. Inorg. Nucl. Chem.*, **40**, 195 (1978). i) At 48 °C. j) Indiscernible because of poor solubility of the complex.

TABLE 9. $^{13}C\{^1H\}$ FT NMR DATA IN $CDCl_3$ FOR THE MIXED-LIGAND CHELATES[a]

No.	β-dik	δ [J(Pt-C)] (J (F-C))				
		CH_3	CF_3	CH	CH_3CO	CF_3CO
1n	acac	24.9		101.7	186.7, 187.5	
	tfac	27.2	116.3q (283)	97.5	195.1	168.2q (34)
1o	acac	24.4		101.8	187.0	
	hfac		115.6q (283)	92.6m (1.7)		175.0q (37)
2n	acac	25.2 [46]		103.1 [74]	185.5, 186.4 [26] [27]	
	tfac	27.3 [41]	116.5q [63](282)	99.5 [72]	192.4 [24]	165.9q [21](34)
2o	acac	24.8 [48]		103.1 [74]	186.7 [27]	
	hfac		116.3q [62](283)	95.8m [73](1.8)		171.5q [22](36)

a) Chemical shifts in ppm from internal Me_4Si and the J(Pt–C) in brackets and J(F–C) in parentheses in Hz.

TABLE 10. $^{19}F\{^1H\}$ NMR DATA[a]

No.	Solvent	δ [J(Pt–F)]
1d[b]	CH_2Cl_2	−73.8
1h[c]	$CDCl_3$	−69.5(*cis*), −69.6(*trans*)[d]
2d[b]	CH_2Cl_2	−73.8[17]
2h-*cis*[c]	$CDCl_3$	−69.8[18]
2h-*trans*[c]	$CDCl_3$	−69.9[18]

a) Chemical shifts in ppm downfield from $CFCl_3$ and the J (Pt–F) values in brackets in Hz. b) The chemical shifts were measured to be 4.68 and 4.74 ppm from external CF_3COOH for **1d** and **2d**, respectively, and converted to the $CFCl_3$ reference by means of the equation, $\delta_{CFCl_3}=\delta_{CF_3COOH}-78.5$ppm. c) The chemical shifts were measured from external C_6F_6[6] and converted to values referring to $CFCl_3$ by virtue of $\delta_{CFCl_3}=\delta_{C_6F_6}-162.9$ ppm. d) The more intense signal was assigned to *trans*.

in C_6D_6, the more intense upfield signal of **1h** was assigned to the *trans* isomer (Table 6) in accordance with the information from IR spectrum that crystalline **1h** is *trans* (Fig. 3). The ^{19}F NMR data for **1h** as compared with those for **2h** are consistent with this assignment, the more intense *trans* signal appearing in slightly higher field than the *cis* signal (Table 10).

The chemical shifts of methine protons in *cis*- and *trans*-[Pd(bzac)$_2$] (**1g**) are slightly different from each other in $CDCl_3$. Isomerization reaction between them was followed by virtue of these signals and found to attain equilibrium at [*cis*]/[*trans*]=2/1 within one day. Both isomers of **1g** also show different ^{13}C chemical shifts except for some of the benzoyl carbons (Table 8). The ^{13}C NMR spectrum of orange plates of [Pd(hxd)$_2$] (**1f**) in $CDCl_3$, which were assumed to be *cis* based on the IR spectra, changed with time to attain equilibrium after *ca.* 6 h at the isomer ratio of 1 : 1. The ^1H NMR spectra of [Pd(etac)$_2$] (**1i**) showed signal splitting for the acetyl methyl and $C\underline{H}_2$–CH_3 protons in $CDCl_3$ but only for the CH_2–$C\underline{H}_3$ protons in C_6D_6. The more abundant species in $CDCl_3$ was tentatively assigned to *trans* by reference to the previous studies on the d^8-metal chelates of *O*-ethyl 3-thioxobutanethioate.[26] Isomerization of **1i** in $CDCl_3$ is rapid, attaining equilibrium within 10 min at −40 °C.[4] The ^1H NMR spectrum of [Pd(etbz)$_2$] (**1k**) also shows coexistence of *cis* and *trans* isomers in $CDCl_3$.

Assignment of the ^1H and ^{13}C NMR signals for the mixed-ligand chelates to each β-diketonate ligand (Tables 7 and 9) was made by reference to the data for the respective binary bis-chelates. Methyl protons of the acac ligand in [M(acac)(tfac)] (**1n** and **2n**) exhibit two signals in C_6D_6 due to the unsymmetric nature of tfac. Unambiguous assignment of these signals to the two unequivalent methyl groups is difficult, since the *trans* influence of the trifluoroacetyl part relative to the other acetyl part of the tfac ligand is not certain on the basis of the present ^1H NMR data. Thus in C_6D_6, the methyl protons in [Pt(acac)(hfac)] (**2o**) resonate at 0.08 ppm upfield compared with those in [Pt(acac)$_2$] (**2a**), whereas the methyl protons in *cis*-[Pt(tfac)$_2$] (**2h**) resonate at 0.07 ppm downfield compared with those in the *trans* isomer, and the methyl signals for *cis*-[Pd(tfac)$_2$] (**1h**) are observed at 0.04 ppm lower field than those for *trans*.

The mixed-ligand palladium(II) and platinum(II) chelates are rather stable in solution, showing no appreciable change in their ^1H NMR spectra even after one month. On the other hand, refluxing of dichloromethane or methanol solution of two kinds of bis-chelates did not give rise to the mixed-ligand chelates, whereas the ligand exchange reactions have been reported for many β-diketonate chelates of Cu(II), Al(III), In(III), Ce(IV), Ti(IV), Zr(IV), Hf(IV), V(IV), Fe(III), Co(III), and Ni(II).[2] Thus the geometrical isomerization of bis(unsymmetric β-diketonato)palladium(II) complexes seems to proceed *via* a reaction pathway other than the intermolecular mechanism.

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