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Reactions of the Bis(β-diketonato)platinum(II) Complexes with Various Nitrogen Bases**

Seichi Okeya,*,† Yukio Nakamura, and Shinichi Kawaguchi*

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

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

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The bis(β-diketonato)platinum(II) complexes react with various nitrogen bases (L) to afford $[\mathrm{Pt}(\beta\text{-dik})\mathrm{L}_2](\beta\text{-dik})$, $[\mathrm{Pt}(\beta\text{-dik-}O)_2\mathrm{L}_2]$, $[\mathrm{PtL}_4](\beta\text{-dik})_2$, and $[\mathrm{Pt}(\beta\text{-dik})(\beta\text{-dik-}C)\mathrm{L}]$ depending on the natures of the β-diketonate anions and L. All of these complexes are stable in solution, showing no sign of isomerization and dissociation of L. The platinum(II) complexes containing the *O*-unidentate β-diketonate ligand are much more stable than the corresponding palladium(II) complexes and $[\mathrm{Pt}(\mathrm{acac})(\mathrm{piperidine})_2](\mathrm{acac})$ and $[\mathrm{Pt}(\mathrm{acac\text{-}}O)_2(\mathrm{piperidine})_2]$ constitute a pair of linkage isomers. The complexes containing the 2,4-pentanedionate anion (acac) in the outer sphere readily undergo the H-D exchange of the methine proton of acac and the NH protons of coordinated amines with $\mathrm{CDCl_3}$.

Bis(β-diketonato)palladium(II) complexes $[\mathrm{Pd}(\beta\text{-dik})_2]$ are labile and undergo facile substitution reactions with ammonia, alkylamines, and heterocyclic nitrogen bases (L)[1,2] to afford complexes of the type $[\mathrm{Pd}(\beta\text{-dik})\mathrm{L}_2](\beta\text{-dik})$ (**4**), $[\mathrm{PdL}_4](\beta\text{-dik})_2$ (**5**), $[\mathrm{Pd}(\beta\text{-dik})(\beta\text{-dik-}C)\mathrm{L}]$ (**7**), and $[\mathrm{Pd}(\beta\text{-dik-}C)_2\mathrm{L}_2]$ (**8**), whereas reactions with aniline and its derivatives give rise to the anilide-bridged dinuclear complexes.[3] The reactions of $[\mathrm{M}(\beta\text{-dik})_2]$ (M=Pd and Pt) with tertiary phosphines have also been studied and five-coordinate complexes $[\mathrm{M}(\mathrm{hfac})_2(\mathrm{PR}_3)]$ (**2**)[4] as well as the complexes containing *O*-unidentate β-dik ligands $[\mathrm{M}(\beta\text{-dik})(\beta\text{-dik-}O)(\mathrm{PR}_3)]$ (**3**) and $[\mathrm{M}(\beta\text{-dik-}O)_2(\mathrm{PR}_3)_2]$ (**6**) were isolated and characterized[5] besides complexes **4**, **5**, and **7**. This investigation demonstrated some differences between palladium(II) and platinum(II) in preference of the coordination modes of β-dik anions, and the present paper reports the supplementary study on the reactions of $[\mathrm{Pt}(\beta\text{-dik})_2]$ with nitrogen bases which are to be compared with those of the corresponding $[\mathrm{Pd}(\beta\text{-dik}_2)]$ complexes.

Experimental

Preparation of Complexes. The starting $[\mathrm{Pt}(\beta\text{-dik})_2]$ complexes inclusive of $[\mathrm{Pd}(\mathrm{acac})(\mathrm{tfac})]$ were prepared by the methods reported recently.[6] Gaseous methylamine was evolved from its aqueous solution by addition of potassium hydroxide and condensed in a trap cooled with Dry Ice–methanol. The other amines, pyridines, and ammonia were used as supplied without further purification.

2,4-Pentanedionatobis(piperidine)platinum(II) 2,4-Pentanedionate, $[Pt(acac)(pip)_2](acac)$ (4a), and Bis(2,4-pentanedionato-O)bis(piperidine)platinum(II), $[Pt(acac\text{-}O)_2(pip)_2]$ (6a): $[\mathrm{Pt}(\mathrm{acac})_2]$ (**1a**) (306 mg, 0.778 mmol) was placed in piperidine (519 mg, 6.10 mmol) and stirred at 70 °C for 15 min. The complex was dissolved gradually to produce a new white precipitate of **6a**, which was filtered and washed with benzene followed by dichloromethane. The yield was 86 mg (20%). Compound **6a** is hardly soluble in usual solvents such as benzene, chloroform, methanol, and dimethyl sulfoxide, but can be recrystallized from a mixture (1:1 by volume) of chloroform and methanol.

The filtrate was concentrated by evaporation at 50—60 °C under reduced pressure to leave a pale yellow oil, which, on standing in the atmosphere, crystallized in plates. The solid mass was washed several times with small portions of hexane to obtain a white powder of **4a** (329 mg) in a 75% yield. Contrary to **6a**, compound **4a** is soluble in various solvents such as benzene, dichloromethane, diethyl ether, and acetone. Recrystallization from hexane gave the monohydrate as white needles, while an acetone solution produced anhydrous crystals.

$[Pt(hfac)(Et_2NH)_2](hfac)$ (4b) and $[Pt(hfac)(pip)_2](hfac)$ (4c): Diethylamine (44 mg, 0.60 mmol) was added to a diethyl ether solution (3 cm^3) of $[\mathrm{Pt}(\mathrm{hfac})_2]$ (**1b**) (122 mg, 0.200 mmol) and the solvent was evaporated spontaneously at room temperature to leave yellow plates on the wall of reaction vessel. The yield of **4b** was 144 mg (95%). A similar reaction of **1b** with a twice molar amount of piperidine in diethyl ether gave yellow plates of **4c** in a 95% yield.

$[Pt(hfac)(2\text{-}CH_3C_6H_4NH_2)_2](hfac)$ (4d): A mixture of **1b** (72 mg, 0.12 mmol) and 2-methylaniline (25 mg, 0.23 mmol) was allowed to react in benzene (3 cm^3) at ambient temperature for two days. The solvent was then removed under reduced pressure and the residue was extracted with dichloromethane. Hexane was added to the extract and the mixture was kept in a refrigerator to deposit yellow cubes (63 mg) in a 64% yield.

$[Pt(hfac)(Ph_2en)](hfac)$ (4e): On addition of an equimolar amount of *N,N'*-diphenylethylenediamine to a solution of **1b** in dichloromethane, a white crystalline precipitate of **4e** appeared immediately in a quantitative yield. Compound **4e** is sparingly soluble in usual solvents.

$[Pt(acac)(Et_2NH)_2](tfac)$ (4f) and $[Pt(acac)(pip)_2](tfac)$ (4g): A mixture of $[\mathrm{Pt}(\mathrm{acac})(\mathrm{tfac})]$ (50 mg, 0.11 mmol) and diethylamine (3 cm^3) was heated under reflux for 2 h, when a tiny amount of white precipitate appeared, which was separated by filtration but was insufficient to be identified. The solvent was removed under reduced pressure to leave a yellow crystalline solid, which was recrystallized from a mixture (1:1 by volume) of dichloromethane and petroleum ether to afford colorless columns (20 mg) of **4f** in a 31% yield. Complex **4g** was also prepared in a manner similar to **4f** and recrystallization from benzene–petroleum ether gave colorless plates in a 22% yield.

Tetrakis(propylamine)platinum(II) 2,4-Pentanedionate Monohydrate, $[Pt(n\text{-}PrNH_2)_4](acac)_2\cdot H_2O$ (5a): A mixture of **1a**

** In this paper the chelated, single oxygen bonded, and central carbon bonded anions of β-diketones (β-dikH) such as 2,4-pentanedione (acacH), 1,1,1-trifluoro-2,4-pentanedione (tfacH), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) are represented by β-dik, β-dik-*O*, and β-dik-*C*, respectively, and β-dik in the outer sphere shows a counter ion. Other abbreviation: pip, piperidine; $\mathrm{Ph_2en}$, *N,N'*-diphenylethylenediamine; $\mathrm{CyNH_2}$, cyclohexylamine.

(200 mg, 0.509 mmol) and propylamine (5 cm^3) was heated under reflux for 10 min and cooled then to −5 °C to deposit colorless plates, which were filtered and washed with diethyl ether. The yield was 155 mg (47%).

$[\mathrm{Pt(en)_2}](\mathrm{acac})_2\cdot\mathrm{H_2O}$ (5b): When a mixture of **1a** (168 mg, 0.427 mmol) and ethylenediamine (3 cm^3) was heated to about 80 °C for 3 h, a white precipitate appeared and increased gradually. The mixture was cooled spontaneously to room temperature and acetone (5 cm^3) was added to it. The precipitate was filtered and washed with acetone. Recrystallization from methanol–acetone gave white needles (163 mg) in a 72% yield.

$[\mathrm{Pt(CyNH_2)_4}](\mathrm{tfac})_2$ (5c) and $[\mathrm{Pt(CyNH_2)_4}](\mathrm{hfac})_2$ (5e): After the reaction of $[\mathrm{Pt(tfac)_2}]$ (**1c**) (50 mg, 0.10 mmol) with cyclohexylamine (0.5 cm^3) at about 80 °C for 10 min, diethyl ether (1 cm^3) was added to the cooled reaction mixture to deposit a white precipitate, which was filtered and washed with diethyl ether. The yield was 33 mg (37%). A similar reaction between **1b** and cyclohexylamine gave a white powder of **5e** in a 40% yield. Compounds **5c** and **5e** are both sparingly soluble in usual solvents.

$[\mathrm{Pt(py)_4}](\mathrm{tfac})_2\cdot 3\mathrm{H_2O}$ (5d): A white precipitate appeared immediately after dissolution of **1c** (46 mg, 0.092 mmol) in pyridine (0.5 cm^3). A small portion of hexane was added to the mixture, which was cooled to −5 °C. The precipitate was filtered and washed with diethyl ether. The yield was 79 mg (74%). Recrystallization from dichloromethane–petroleum ether gave white needles.

$[\mathrm{Pt(2\text{-}CH_3C_6H_4NH_2)_4}](\mathrm{hfac})_2\cdot(\mathrm{CH_3})_2\mathrm{CO}$ (5f): 2-Methylaniline (32 mg, 0.30 mmol) was added to a solution of **1b** (45 mg, 0.074 mmol) in benzene (1 cm^3) and the mixture was stirred for 3 h. The solvent was removed under reduced pressure to leave a yellow crystalline solid, which was washed with diethyl ether. The yield was 69 mg (90%). Recrystallization from acetone–hexane gave white needles which contain an acetone molecule per platinum in crystals.

$[\mathrm{Pt(py)_4}](\mathrm{hfac})_2$ (5g): Complex **1b** (80 mg, 0.13 mmol) reacted with pyridine (0.3 cm^3) in an exothermic fashion to result in an orange solution. Gradual addition of diethyl ether (1 cm^3) followed by hexane (5 cm^3) to the solution precipitated white needles, which were filtered and washed with a mixture (1:1 by volume) of diethyl ether and hexane. The yield was 103 mg (86%).

$[\mathrm{Pt(4\text{-}CN\text{-}py)_4}](\mathrm{hfac})_2$ (5h): On addition of eight times molar 4-cyanopyridine to a benzene solution of **1b**, a yellow crystalline precipitate appeared immediately, which was filtered and washed with diethyl ether. The yield was almost quantitative. Compound **5h** is sparingly soluble in usual solvents.

$[\mathrm{Pt(bpy)_2}](\mathrm{hfac})_2$ (5i): 2,2′-Bipyridine (54 mg, 0.35 mmol) was added to a solution of **1b** (104 mg, 0.171 mmol) in dichloromethane (2 cm^3) and the mixture was left to stand to deposit a yellow crystalline precipitate, which was filtered and washed with diethyl ether. The yield was 123 g (78%).

Bis(diethylamine)bis(1,1,1-trifluoro-2,4-pentanedionato-O)platinum(II), $[\mathrm{Pt(tfac\text{-}O)_2(Et_2NH)_2}]$ (6b), and $[\mathrm{Pt(tfac\text{-}O)_2(pip)_2}]\cdot\mathrm{H_2O}$ (6c): A twice molar amount of diethylamine or piperidine was added to a dichloromethane solution of **1c** and the solvent was evaporated spontaneously. The residue was washed with dichloromethane to leave a white crystalline solid. The yields of **6b** and **6c** were 14 and 19%, respectively. Solubilities of both complexes in usual solvents are low.

1,1,1-Hexafluoro-2,4-pentanedionato(1,1,1-hexafluoro-2,4-pentanedionato-C^3)(2-methylaniline)platinum(II), $[\mathrm{Pt(hfac)(hfac\text{-}C^3)(2\text{-}CH_3C_6H_4NH_2)}]$ (7a): 2-Methylaniline (24 mg, 0.22 mmol) was added to a solution of **1b** (120 mg, 0.200 mmol) in benzene (5 cm^3) and the mixture was refluxed for 8 h. The solvent was then removed under reduced pressure and the residue was recrystallized from hexane to give yellow cubes (45 mg) in a 31% yield.

Bis(4-methylamino-1,1,1,5,5,5-hexafluoro-3-penten-2-onato)platinum(II), $[\mathrm{Pt\{N(CH_3)C(CF_3){=}CHCOCF_3\}_2}]$ (11): When methylamine (3 cm^3) was added to a solution of **1b** (120 mg, 0.200 mmol) in diethyl ether (5 cm^3), color of the solution changed from orange to red. The solvent was evaporated spontaneously to leave a red oil and a red crystalline solid. The mixture was dissolved in dichloromethane and recrystallized by addition of petroleum ether to give red needles (32 mg) in a 25% yield. Found: C, 22.70; H, 1.30; N, 4.51%. Calcd for $\mathrm{C_{12}H_8N_2O_2F_{12}Pt}$: C, 22.69; H, 1.27; N, 4.41%. Sublimation temp: *ca.* 120 °C. IR in Nujol (cm^{-1}): $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})+\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})+\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, 1627 vs, 1602 s, 1545 vs, 1515 m; ν(C–F), 1230 vs, 1195 vs, 1138 vs. ^{1}H NMR in CDCl$_3$ (δ, ppm from internal Me$_4$Si): 3.45 q (3H, NCH$_3$, $^5J(\mathrm{F{-}H})=2$ Hz, $^3J(\mathrm{Pt{-}H})=27$ Hz), 5.99 s (1H, CH, $^4J(\mathrm{Pt{-}H})=6$ Hz).

Measurements. IR spectra were recorded in Nujol mull on Hitachi EPI-S2 and 295 spectrophotometers. NMR spectra were measured with JEOL JNM-C60HL and -MH100 (for ^{1}H), FX60Q (for ^{1}H and ^{13}C), and PS-100 (for ^{19}F) instruments.

Results and Discussion

Reactions of $[\mathrm{Pt}(\beta\text{-dik})_2]$ (β-dik=acac (**1a**), hfac (**1b**), and tfac (**1c**)) inclusive of [Pt(acac)(tfac)] with several kinds of nitrogen bases have been examined. In general primary amines and pyridines gave complexes of type **5**, while secondary amines **4** and/or **6**. The reaction between **1b** and 2-methylaniline was exceptional, giving three types of complexes **7a**, **4d**, and **5f** depending on the reactants mole ratio, but did not produce the anilide-bridged dinuclear complexes in contrast with the reactions of $[\mathrm{Pd(hfac)_2}]$ with aniline and its derivatives.[3]

Complexes **1a** and **1c** did not react with bubbling ammonia in dichloromethane solutions, while **1b** gave a minute amount of unidentified product. A solution of **1a** in methylamine showed no sign of reaction up to the boiling point. When **1b** and **1c** were dissolved in methylamine and propylamine, red solutions resulted indicating occurrence of reactions, but no reproducible product has been obtained except **11**. A Schiff base complex $[\mathrm{Pt\{N(CH_3)C(CF_3){=}CHCOCF_3\}_2}]$ (**11**) was isolated from the reaction mixture of **1b** and methylamine in diethyl ether and characterized as described in the Experimental Section. A similar palladium(II) Schiff base complex was also obtained by the reaction of $[\mathrm{Pd(tfac)_2}]$ with aniline.[3]

Table 1 presents the analytical data for newly prepared complexes and Table 2 the IR data for representative ones among them. Similarly to the case of palladium(II) complexes,[1] the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})+\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ bands in the 1800—1500-cm^{-1} region are helpful in diagnosing the bonding modes of the β-dik anions. Thus complexes **5** exhibit bands caused by β-dik anions in the outer sphere, but **4** additional bands assignable to the chalating β-dik ligands. Complexes

Table 1. Newly prepared complexes, $[Pt(\beta\text{-dik})L_2](\beta\text{-dik})$ (**4**), $[PtL_4](\beta\text{-dik})_2$ (**5**), $[Pt(\beta\text{-dik-}O)_2L_2]$ (**6**), and $[Pt(\beta\text{-dik})(\beta\text{-dik-}C)L]$ (**7**)

Compd	β-dik	L	Decomp temp / °C	Found (Calcd) (%) C	H	N
4a	acac	pip	*ca.* 169	42.68(42.62)	6.50(6.44)	4.92(4.97)
4a[a)]	acac	pip	69— 70 (mp)	41.32(41.30)	6.49(6.59)	4.56(4.82)
4b	hfac	Et_2NH	*ca.* 65	28.94(28.62)	3.33(3.20)	3.92(3.71)
4c	hfac	pip	161—162	30.59(30.82)	3.00(3.10)	3.52(3.59)
4d	hfac	ma[b)]	*ca.* 135	34.99(35.00)	2.44(2.45)	3.33(3.40)
4e	hfac	½Ph_2en	195—200	35.04(35.09)	2.20(2.21)	3.57(3.41)
4f[c)]	acac tfac	Et_2NH	*ca.* 100 (mp)	35.95(36.42)	5.58(5.60)	4.48(4.72)
4g[c)]	acac tfac	pip	175—177	38.91(38.89)	5.32(5.39)	4.37(4.54)
5a[a)]	acac	*n*-$PrNH_2$	184—186	42.32(41.96)	8.18(8.00)	9.38(8.90)
5b[a)]	acac	½en	*ca.* 205	31.06(31.63)	6.03(6.07)	10.55(10.54)
5c	tfac	$CyNH_2$	183—185	44.99(45.48)	6.90(6.74)	6.34 (6.24)
5d[d)]	tfac	py	*ca.* 132	41.36(41.33)	3.81(3.93)	6.30 (6.43)
5e	hfac	$CyNH_2$	197—200	41.21(40.60)	5.62(5.41)	5.14 (5.57)
5f[e)]	hfac	ma[b)]	*ca.* 151	44.99(44.93)	4.02(4.05)	5.12 (5.11)
5g	hfac	py	*ca.* 195	39.15(38.93)	2.52(2.40)	6.06 (6.06)
5h	hfac	4-CN-py	*ca.* 185	39.97(39.81)	1.76(1.77)	11.02(10.93)
5i	hfac	½bpy	157—164	38.62(39.10)	2.08(1.97)	6.06 (6.08)
6a	acac	pip	*ca.* 150	42.45(42.62)	6.53(6.44)	4.70 (4.97)
6b	tfac	Et_2NH	167—171	33.10(33.28)	4.70(4.97)	4.14 (4.34)
6c[a)]	tfac	pip	*ca.* 180	34.90(34.94)	4.40(4.69)	3.97 (4.07)
7a	hfac	ma[b)]	134—135	28.56(28.50)	1.60(1.55)	2.02 (1.96)

a) Monohydrate. b) 2-Methylaniline. c) The acac anion chelating. d) Trihydrate. e) Containing one acetone molecule per metal atom.

Table 2. Characteristic IR bands of representative complexes in Nujol mull

Compd	ν(NH)/cm^{-1}	ν(C$\cdots$C) + ν(C$\cdots$O)/cm^{-1}
4a	3057 s	1610 vs, 1570 vs, 1550 s, 1525 vs, 1503 vs
4d	3180m, 3050 s	1670 s, 1600 vs, 1553 m, 1535 s
4g	3100 s	1640 s, 1565 vs, 1540 vs, 1520 vs
5a	3150 s, 3100 s	1602 vs, 1504 vs
5d		1635 vs, 1550 vs, br
5f	3210 s, 3020 s	1670 vs, 1520 vs
5g		1676 vs, 1573 m, 1530 vs, br
6a[a)]	3170 vs,	1621 vs, 1583 w
6b[b)]	3200 vs,	1649 vs
7a	3226m, 3148w	1752 vs, 1703 m, 1598 vs, 1573 s, 1560 s, 1536 m, 1505 m

a) The 1621 and 1583 cm^{-1} bands are assigned to vibrations of the localized C=O and C=C bonds, respectively. The ν(C–O) band is observed at 1165 cm^{-1} (vs). b) The 1649 cm^{-1} band is assigned to ν(C=O). The ν(C–O) band is indiscernible because of overlapping with strong ν(C–F) bands.

6a—**c** are the first examples of complexes composed of the *O*-unidentate β-dik and amines. The ν(C=O) frequencies for **6a** and **6b** are lower by about 30 and 10 cm^{-1}, respectively, than those for the corresponding triethylphosphine complexes, *trans*-$[Pt(acac\text{-}O)_2(PEt_3)_2]$ (1650 cm^{-1})[7)] and *trans*-$[Pt(tfac\text{-}O)_2(PEt_3)_2]$ (1660 cm^{-1}).[5)] The intramolecular or intermolecular hydrogen-bonding interaction between the dangling acetyl or trifluoroacetyl group and the amine group might be responsible for the lower frequency shift of the ν(C=O) band for the present complexes **6**.

^{1}H and ^{13}C NMR Spectra. Tables 3 and 4 list the ^{1}H NMR data for the present complexes except sparingly soluble ones. The ^{13}C NMR data for representative complexes are given in Table 5. They are quite similar to those for the corresponding palladium(II) complexes,[1)] and couplings of ^{1}H and ^{13}C atoms to ^{195}Pt are very helpful in diagnosing the bonding states of β-dik anions in the present case. Complexes **5** exhibit each one set of ^{1}H and ^{13}C NMR signals from β-dik anions. All signals lack coupling to ^{195}Pt, indicating that the β-dik anions are involved as counter anions in the outer sphere. Complexes **4**, on the other hand, show each two sets of ^{1}H and ^{13}C signals from β-dik anions. Signals from the chelating β-dik are flanked by the ^{195}Pt satellites and easily distinguished from those assignable to β-dik in the outer sphere. The ^{13}C shieldings and the ^1J(C–H) and J(C–F) values for hfac anions in the outer sphere of **4c** and **5g** are quite similar to those obtained for [K(18-crown-6)](hfac)[1)] and [{1,8-bis(dimethylamino)-naphthalene}H](hfac).[3)] The ^{19}F NMR spectrum of **5g** in dichloromethane shows a singlet at 4.70 ppm downfield from external CF_3COOH without coupling to ^{195}Pt.

In spite of the salt-like compositions, complexes **4** and **5** as well as the corresponding palladium(II) complexes[1)] are generally more soluble in aprotic or-

TABLE 3. ^{1}H NMR DATA FOR [PtL$_4$](β-dik)$_2$ (**5**) AND [Pt(acac-*O*)$_2$(pip)$_2$] (**6a**)a)

Compd	Solvent	β-dik		L	
		CH_3	CH	NH_2	Other
5a	$CDCl_3$	1.70	5.06b)	6.29 br {59}	*n*-Pr: 2.54 m, br, 1.59 m, 0.86 t(7)
	C_6D_6	1.91	5.40	6.76 br {*ca.* 60}	*n*-Pr: 2.69 m, br, 1.8 m, 0.95 t(7)
5b	D_2O	2.07	b)	b)	CH_2: 2.64{41}
5d	$CDCl_3$	2.23	5.62		py: 9.70 dd(6 and 2){41}, 7.4 br (H_2O: 2.50)
5f	$(CD_3)_2CO$		5.67	7.65 br {c)}	CH_3: 2.23, Ph: 6.96, 6.91
5g	$CDCl_3$		5.95		py: 9.72 dd(6 and 2){41}, 7.3—7.8 m
5i	$(CD_3)_2CO$		5.45		bpy: $H^{3,3'}$ 8.76 dd, $H^{4,4'}$ 8.41 dt, $H^{5,5'}$ 7.73 ddd, $H^{6,6'}$ 9.26 d{28} ($J_{3,4}=8$, $J_{3,5}=$ *ca.* 2, $J_{4,5}=8$, $J_{4,6}=$ *ca.* 1, and $J_{5,6}=6$)
6a	$CDCl_3+CD_3OD$ (1:1 by volume)	2.34 {5} 2.25	6.92 {12}	4.1_3 brd)	pip: $H^{2,6}$(eq) 3.1_3 br, $H^{2,6}$(ax) 2.7_4 br, $H^{3,4,5}$ 1.58 br

a) Chemical shifts in ppm from internal Me_4Si except those in D_2O from internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate. Figures in parentheses and braces give *J*(H-H) and *J*(Pt-H) in Hz, respectively. d = Doublet, dd = doublet of doublets, ddd = doublet of double doublets, dt = doublet of triplets, m = multiplet, and br = broad. b) The H-D exchange occurs with the solvent. c) Indiscernible. d) NH proton.

TABLE 4. ^{1}H NMR DATA FOR [Pt(β-dik)L$_2$](β-dik) (**4**) AND [Pt(hfac)(hfac-*C*^{3})(2-$CH_3C_6H_4NH_2$)] (**7a**)a)

Compd	Solvent	β-dik(IS)		β-dik(OS)		Lc)	
		CH_3	CH	CH_3	CH	NH	Other
4a	$CDCl_3$	1.88{*ca.* 4}	5.38{8}	1.84	5.13b)	b)	pip: 3.4, 2.7, 1.5
	CD_2Cl_2	1.84{4}	5.45{8}	1.80	5.11	8.21{78}	pip: 3.6, 2.7, 1.5
	$(CD_3)_2CO$	1.83{4}	5.59{8}	1.72	4.99b)	8.4_2b)	pip: 3.3, 2.6, 1.4
	C_6D_6	1.44{*ca.* 3}	4.97{8}	2.12	5.52	8.85{*ca.* 80}	pip: 3.7, 2.7, 1.9, 1.2
4b	$CDCl_3$		6.29{7}		5.70	7.8_8{*ca.* 70}	Et: *ca.* 2.8 m, 1.43 t(7)
4c	$CDCl_3$		6.34{7}		5.91	7.75{78}	pip: 3.4, 2.6, 1.50
	C_6D_6		5.85{7}		6.36	7.77{83}	pip: 3.23, 2.31, 1.4_8, 1.11
4d	$CDCl_3$		6.03{8}		5.79	7.3_3{75}	CH_3: 2.33, Ph: 7.1 m
4f	$CDCl_3$	1.83{4}	5.44{8}	2.06	5.37	$7._5${*ca.* 80}	Et: 2.7 m, 1.44 t(7)
4hd)	$CDCl_3$	1.96{4}	5.68{8}	2.32	5.20		py: $H^{2,6}$ 8.46 dd(6 and 2) {44}, H^4 8.0 m, br, $H^{3,5}$ 7.5 m, br
7a	$CDCl_3$		6.21{7}		5.99e) {120}	5.72 {*ca.* 80}	CH_3: 2.28, Ph: 7.1 m

a, b) Same as footnotes a) and b) for Table 3. IS and OS abbreviate inner and outer spheres, respectively. c) The NH-proton signals are all broad. Chemical shifts for the piperidine protons refer to $H^{2,6}$(equatorial), $H^{2,6}$(axial), and $H^{3,5}$(equatorial) plus H^4 in this sequence and those for $H^{3,5}$(axial) are indiscernible except in the case of **4a** (δ 1.9) and **4c** (δ 1.4_8) in C_6D_6. d) [Pt(acac)(py)$_2$](tfac) (**4h**) was obtained as an oily substance from the reaction of [Pt(acac)(tfac)] with twice molar pyridine in dichloromethane at room temperature. e) Methine of the carbon-bonded hfac.

ganic solvents such as dichloromethane and benzene rather than in water. The amine groups which are the most hydrophilic part in the complex cations might be shielded by the hydrocarbon moiety of the β-dik anion in the outer sphere *via* the hydrogen bonding with the carbonyl oxygens as revealed by the X-ray analysis of [Pd(acac)(Et$_2$NH)$_2$](acac) at −170 °C.[8)] The fact that the NH proton of piperidine in **4a** resonates at downfield by 4 ppm as compared with that in **6a**, isomer of **4a**, also reflects the effect of hydrogen bonding with the acac anion in the outer sphere which is much stronger than the intramolecular interaction in **6a**. Complex **5b** as well as [Pd(NH$_3$)$_4$](β-dik)$_2$[1)] is exceptional, which is readily soluble in water but not in organic solvents. In these complexes the ammine and amine protons may not be sufficiently shielded by the counter anions.

As is noticed in Tables 3 and 4, C_6D_6 exhibits a remarkable effect on the ^{1}H NMR spectra of complexes **4** and **5**. Signals from the chelating β-dik are shifted upfield by about 0.5 ppm and those from β-dik in the outer sphere are shifted downfield by

TABLE 5. ^{13}C NMR DATA FOR SOME REPRESENTATIVE COMPLEXES[a)]

Compd	Solvent	β-dik(IS)			β-dik(OS)			L		
		CH_3 or CF_3	CH	CO	CH_3 or CF_3	CH	CO	C^α	C^β	C^γ
4a	$CDCl_3$	26.6 (128) {33}	102.5 (159) {57}	184.3 {21}	29.0 (125)	97.5 (149)	187.7	53.4 (140) {30}	26.2 (127) {47}	24.3 (126) {8}
4c	$CDCl_3$	116.8q [283] {b)}	95.6 (168) {66}	170.8q [36] {b)}	118.0q [290]	86.3 (161)	175.4q [32]	54.1 (141) {32}	25.9 (128) {47}	23.5 (129) {7}
	C_6D_6	117.3q [283] {b)}	95.7 (168) {66}	170.3q [36] {*ca.* 20}	119.0q [290]	87.0 (161)	176.1q [32]	54.3 (141) {32}	26.2 (130) {51}	23.6 (130) {7}
5a	$CDCl_3$				28.6 (125)	97.4 (152)	187.3	50.2 (139) {23}	24.0 (128) {53}	11.6 (127)
5b	D_2O				28.1 (126)	c)	195.5	47.6 (143) {5}		
5g	$CDCl_3$				118.6 [292]	84.9 (160)	174.3q [30]	153.0 (185)	126.9 (170) {44}	139.5 (189) {12}

6a in a mixture (1:1 by volume) of $CDCl_3$ and CD_3OD

β-dik[d)]					pip		
C^1	C^2	C^3	C^4	C^5	C^α	C^β	C^γ
23.9 {b)}	188.7 {21}	103.3 {22}	196.8	30.6	53.4 {*ca.* 19}	26.7 {32}	23.9

a) Chemical shifts in ppm from internal Me_4Si except those for **5b** in D_2O which are referred to internal dioxane (δ 67.4). Figures in parentheses, braces, and brackets give *J*(C-H), *J*(Pt-C), and *J*(F-C) in Hz, respectively. q=Quartet. b) Indiscernible. c) Indiscernible because of H-D exchange. d) Numbering of the carbon atoms: $PtOC^2(C^1H_3)C^3HC^4OC^5H_3$.

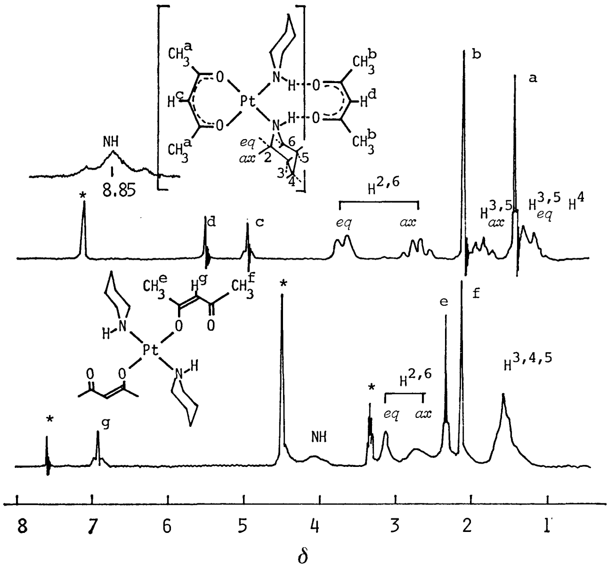

Fig. 1. The proposed structures and the ^{1}H NMR spectra of [Pt(acac)(pip)$_2$](acac) (**4a**) in C_6D_6 and [Pt(acac-*O*)$_2$(pip)$_2$] (**6a**) in $CDCl_3+CD_3OD$ (1:1 by volume) at 100 MHz with internal Me_4Si. The asterisks denote the peaks due to solvent impurities.

0.2—0.5 ppm as compared with those in other solvents. Thus the methine signals for β-dik anions in the inner and outer spheres of **4a** and **4c** interchange their relative positions in $CDCl_3$ and C_6D_6. On the other hand, such a kind of solvent effect is not observed for ^{13}C NMR spectra of **4c** (Table 5). Similar phenomena were found for the corresponding palladium(II) complexes and attributed to the anisotropic magnetic effect of benzene molecules.[1)]

Solubilities of complexes **6** in organic solvents are very low but fortunately **6a** dissolves in a mixture (1:1 by volume) of $CDCl_3$ and CD_3OD sufficiently to allow NMR measurements. The ^{1}H NMR spectrum of **6a** is compared with that of its isomer **4a** in Fig. 1. The spectrum of **4a** involves two methine and two methyl signals, demonstrating that the two acac anions exist in different and both symmetric environments. On the other hand **6a** exhibits one methine signal and two methyl signals, of which the lower-field one is flanked by ^{195}Pt satellites but the higher-field one is not, indicating that the two acac anions in **6a** are environmentally equivalent, but two halves of each acac are not. The ^{13}C NMR spectrum of **6a** (Table 5) also contains only one set of acac signals and three carbons of each acac ligand couple to ^{195}Pt in accordance with the proposed *O*-unidentate structure. Furthermore, these features of NMR spectra indicate that the *O*-unidentate acac ligand has the stereochemically rigid cis configuration around the C=C bond, although $(CH_3)_3Si$(acac-*O*) molecules have either trans or cis enolate acac anion, the latter undergoing rapid head-to-tail fluxional motion.[9)] As to the geometrical structure of **6a**, the trans arrangement as depicted in Fig. 1 is tentatively assigned by the analogy with *trans*-[Pt(acac-

O)$_2$(PEt$_3$)$_2$][7)] and *trans*-[Pt(tfac-O)$_2$(PEt$_3$)$_2$].[5)] The trans structure of the phosphine complexes was indicated by the characteristic quintet resonance of the methyl protons of PEt$_3$ and is also supported by small ^1J(Pt–P) values of 2657 and 2646 Hz observed for [Pt(tfac-O)$_2$(PR$_3$)$_2$] (R=Et and Cy), respectively.[10)]

Complex **4a** is very stable and shows no change on being heated in benzene under reflux for 10 h, whereas complex **6a** decomposes gradually when heated in a chloroform–methanol solution. Thus, though **4a** and **6a** constitute a pair of isomers, interconversion between each other has not been realized. Linkage isomerism is the most interesting and important isomerism in coordination chemistry and a large number of examples have been reported.[11)] Each of **4a** and **6a** is composed of two acac anions and two piperidine molecules. In complex **6a** both acac anions act as the O-unidentate ligand, whereas in **4a** one is serving as a bidentate ligand and the other as a counter ion. Thus the couple of **4a** and **6a** presents a novel type of linkage isomerism.

The ^{1}H NMR spectrum of **7a** in CDCl$_3$ closely resembles that of [Pd(hfac)(hfac-C^3)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NH$_2$)].[3)] Although the J(Pt–H) value (7 Hz) of a methine signal at 6.21 ppm is similar to values observed for chelating β-dik anions in complexes **4** (Table 4), J(Pt–H) for the methine signal at 5.99 ppm is as large as 120 Hz, unequivocally indicating that one hfac anion is carbon-bonded to the metal atom. Metal complexes containing a carbon-bonded hfac anion as a ligand are quite rare,[5)] but similar J(Pt–H) values have been reported for the methine protons of carbon-bonded acac ligands in [Pt(acac)(acac-C^3)L] (110 and 129 Hz for L=PPh$_3$[12)] and py,[13)] respectively) and [Pt(acac-C^3)$_2$(py)$_2$] (102 Hz).[13)]

The H-D Exchange Reactions of Complexes **4** *and* **5** *with CDCl$_3$.* Change with time of ^{1}H NMR spectra of **4a** and **5a** in CDCl$_3$ solutions was followed. Intensities of signals assigned to the acac-methine and NH protons decreased gradually and the CHCl$_3$ signal increased instead to attain equilibria in 30 min (**4a**) and 1 d (**5a**). The corresponding palladium(II) complexes **4a** and **5a** react more rapidly, attaining equilibria in 13 min and several hours, respectively.[1)] The key step of the H-D exchange was supposed to be the proton transfer from the coordinated amine to the acac anion in the outer sphere.[1)] Deprotonation of coordinated amines might be more difficult in the platinum(II) complexes than in the corresponding palladium(II) complexes. The fact that contrary to the case of [Pd(hfac)$_2$],[3)] the reaction of [Pt(hfac)$_2$] with 2-methylaniline in refluxing benzene does not afford the anilide-bridged dinuclear complex but result in **7a** might reflect the same trend. Other complexes **4** and **5** containing tfac and hfac as counter ions do not undergo the H-D exchange in CDCl$_3$ probably because of lower basicities of these anions.

Relative Stabilities in Various Bonding Modes of β-Diketonate Anions. The palladium(II) complexes of the types **4**, **5**, **7**, and **8**, which were prepared by the reactions of [Pd(β-dik)$_2$] with a variety of nitrogen and phophorus bases, are rather substitution labile in solution and attain interconversion equilibria such as $\mathbf{4}\rightleftarrows\mathbf{7}+\mathrm{L}$, $\mathbf{5}\rightleftarrows\mathbf{7}+3\mathrm{L}$, $\mathbf{7}\rightleftarrows\mathbf{1}+\mathrm{L}$, $2\mathbf{7}\rightleftarrows\mathbf{4}+\mathbf{1}$, and $\mathbf{8}\rightleftarrows\mathbf{7}+\mathrm{L}$.[1,5)] On the contrary, the platinum(II) complexes obtained in this study showed no sign of transformation on being kept in solution for a long time or on being heated. It may not be due to the extraordinary inertness, but be ascribed to thermodynamic stability of each platinum(II) complex, since the interconversion between [Pt(acac)(acac-C^3)(py)] and [Pt(acac-C^3)$_2$(py)$_2$] was studied at 40—80 °C.[13)]

Although the reactions between [Pd(β-dik)$_2$] and secondary amines yield only the type-**4** complexes, [Pt(β-dik)$_2$] can afford **6** besides **4**. The O-unidentate linkage of β-dik anions seems to be more favorable to platinum(II) than palladium(II). The same trend was also noticed for reactions of [M(β-dik)$_2$] with tertiary phosphines.[5)] [Pd(hfac)$_2$] reacts with 2,2′-bipyridine (bpy) to produce a type-**4** complex but does not give **5** probably because of the steric requirement of bpy.[1)] On the contrary, [Pt(hfac)$_2$] affords **5i** solely. The discrepancy can not be reasonably rationalized, since the bond radii of palladium(II) and platinum(II) are not appreciably different as shown by X-ray analyses of [Pd(acac)$_2$][14)] and [Pt(acac)$_2$].[15)] It is not certain either why [Pt(tfac)$_2$] does not react with bpy despite that palladium gives [Pd(tfac)(bpy)](tfac).

Preference of the bonding mode is also influenced by the nature of β-dik itself. Piperidine produces both **4a** and **6a** in its reaction with [Pt(acac)$_2$], but gives only **6c** with [Pt(tfac)$_2$] and **4c** with [Pt(hfac)$_2$]. Thus preference of the O-unidentate bonding seems to be in the sequence tfac>acac>hfac. Since tfac is unsymmetric and the charge density may be larger on the acetyl oxygen than on the trifluoroacetyl oxygen, the O-unidentate bonding *via* the acetyl oxygen may not be so unfavorable compared with chelation especially when a good ancillary ligand coexists. On the other hand, chelates of symmetric β-dik anions are much more stable than the O-unidentate state because of not only the chelate effect but also the large electron delocalization effect compared with the case of tfac. Furthermore the least basic hfac anion is a weak ligand and prone to go out of the coordination sphere, the tendency being in the sequence, hfac>tfac>acac. The reactions of [Pt(acac)(tfac)] with secondary amines and pyridine clearly demonstrate this trend, displacing tfac exclusively into the outer sphere to afford [Pt(acac)L$_2$](tfac) (**4f**, **4g**, and **4h**). In a similar way, although pyridine reacts with [Pt(tfac)$_2$] and [Pt(hfac)$_2$] to give **5d** and **5g**, respectively, less basic 4-cyanopyridine can not displace tfac in the former chelate, but does remove hfac ligands in the latter chelate to result in **5h**.

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