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

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Reactions of the bis(β-diketonato)palladium(II) complexes with various nitrogen bases (L) afforded [Pd(β-dik)L_2](β-dik), [PdL_4](β-dik)$_2$, or [Pd(β-dik)(β-dik-*C*)L] according to the natures of L and β-diketonate anions. Less basic ligands such as 1,1,1,5,5,5-hexafluoro- and 1,1,1-trifluoro-2,4-pentanedionates are readily removed by L to the outer sphere. Tendency of preferring the central-carbon-bonded state of the β-diketonate anion is related with the keto-favoring nature of its conjugate acid. Excess primary amines and pyridines can displace both of the β-diketonate ligands but secondary amines only one. These two types of compounds containing the 2,4-pentanedionate anion in the outer sphere undergo prompt deuteration of methine and amine protons by $CDCl_3$. Tribenzylamine and 2,6-diphenylpyridine react with bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)palladium(II) to afford orthometallated products.

β-Dicarbonyl compounds constitute a group of the most popular ligands and usually form the *O,O'*-chelate as a monoanion with almost all metal ions.[1] In recent years, reactions of the bis(β-diketonato)palladium(II) and -platinum(II) complexes with Lewis bases have been examined and found to give products involving the β-diketonate ligand of various bonding modes as shown in Fig. 1. Compounds **7** containing the central-carbon-bonded 2,4-pentanedionate anion (acac-C^3) were obtained by the reactions of [Pd(acac)$_2$] with bases such as pyridine, diethylamine, and triphenylphosphine,[2] but the kinetic and equilibrium studies of the reactions between [Pd(acac)$_2$] and alkylamines revealed that compounds **7** are produced *via* the outer-sphere complex **4**.[3] Primary amines give rise to **5**.[4] Complexes of type **6** were obtained by the reactions of [Pt(acac)$_2$] with piperidine[5] and triethylphosphine,[6] and the precursor complex of type **3** was isolated in the reaction of bis(1,1,1-trifluoro-2,4-pentanedionato)palladium(II), [Pd(tfac)$_2$], with tertiary phosphines.[7] The established examples of **2** are [M(hfac)$_2$L], where hfac stands for an *O,O'*-chelated 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion and L=tri-*o*-tolylphosphine for M=Pd(II) and Pt(II), and L=tricyclohexylphosphine for M=Pt(II).[8] Complexes **8** have been reported for [Pd(etac-C^2)$_2$L$_2$] (L=py, 2-Me-py, $PhCH_2NH_2$, $BuNH_2$, and 1/2bpy)[9] and [Pt(acac-C^3)$_2$(py)$_2$],[10] where etac represents anion of 1-ethoxy-1,3-butanedione (ethyl acetoacetate).

In a previous paper we reported preparation and characterization of the palladium(II) and platinum(II) complexes of various β-dicarbonyl compounds.[11] The present paper is concerned with the reactions of [Pd(β-dik)$_2$] (**1**) with a number of nitrogen bases (L) which are listed in Table 1. Various combinations of L(**a**—**u**) and bis-chelates (**1A**—**1I**) as well as a mixed-ligand chelate [Pd(acac)(tfac)] (**1M**) were examined and especially the reactions of **1A**—**1D** were investigated in detail.

Table 1. β-Diketonate and nitrogen-base ligands used

β-Diketonate anion	Abbr.	Symbol
2,4-Pentanedionate	acac	A
1-Phenyl-1,3-butanedionate	bzac	B
1,1,1-Trifluoro-2,4-pentanedionate	tfac	C
1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate	hfac	D
3-Phenyl-2,4-pentanedionate	Ph-acac	E
1,3-Diphenyl-1,3-propanedionate	dbm	F
2,2,6,6-Tetramethyl-3,5-heptanedionate	dpm	G
1,1,1-Trifluoro-4-(2-thienyl)-2,4-butanedionate	tta	H
1-Ethoxy-1,3-butanedionate	etac	I

Base(L)	Symbol	Base(L)	Symbol
NH_3	a	Bz_3N	*l*
$MeNH_2$	b	py	m
$EtNH_2$	c	2-Me-py	n
n-$PrNH_2$	d	3-Me-py	o
$BzNH_2$	e	4-Me-py	p
½en	f	4-Me_2N-py	q
Me_2NH	g	2,6-Ph_2-py	r
Et_2NH	h	½bpy	s
pip	i	½(4,4'-Me_2-bpy)	t
BzNHMe	j	½(2,9-Me_2-phen)	u
Bz_2NH	k		

a) Bz: benzyl, pip: piperidine, bpy: 2,2'-bipyridine, phen: 1,10-phenanthroline.

Results and Discussion

Table 2 lists decomposition temperature and analytical data of complexes **4**, **5**, and **7** which were obtained by reactions of **1** either with neat liquid L or with L in appropriate solvents. The tendency of nitrogen bases to ligate palladium(II) is very strong and primary amines and pyridines displace both of the β-diketonate ligands to produce complexes **5**. It is difficult to isolate the intermediate products **4** in

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TABLE 2. NEWLY PREPARED COMPLEXES, [Pd(β-dik)L_2](β-dik) (**4**), [PdL_4](β-dik)$_2$ (**5**), AND [Pd(β-dik)(β-dik-*C*)L] (**7**)

Compd	Dec temp °C	Found(Calcd)(%) C	H	N
4Ag[a]	≈r. t.	39.28(39.03)	7.37 (7.49)	6.48 (6.50)
4Ah	86—88	48.00(47.95)	8.15 (8.05)	6.29 (6.21)
4Ai[b]	54—56	48.84(48.73)	7.84 (7.77)	5.68 (5.68)
4Bi	89—91	60.26(60.15)	7.30 (6.73)	5.08 (4.68)
4Cg	*ca.* 75	33.86(33.45)	4.45 (4.41)	5.68 (5.57)
4Ch	*ca.* 64	38.51(38.68)	5.32 (5.41)	4.98 (5.01)
4Ci	*ca.* 130	41.39(41.21)	5.22 (5.19)	4.76 (4.81)
4Cj	*ca.* 133	47.73(47.68)	4.61 (4.62)	4.24 (4.28)
4Ck	106—108	56.52(56.55)	4.72 (4.75)	3.40 (3.47)
4Cs	*ca.* 122	42.01(42.23)	2.79 (2.84)	5.00 (4.93)
4Dg	g)	27.63(27.53)	2.68 (2.64)	4.66 (4.59)
4Di	105—115	34.79(34.77)	3.46 (3.50)	4.06 (4.06)
4Ds	*ca.* 160	35.52(35.30)	1.52 (1.49)	4.11 (4.14)
4Dt	140—145	37.56(37.49)	1.98 (2.00)	4.05 (3.98)
4Du	g)	39.51(39.55)	1.96 (1.94)	3.98 (3.84)
4Mb	*ca.* 92	33.99(34.26)	4.99 (5.03)	6.60 (6.66)
4Mh	*ca.* 85	42.78(42.82)	6.61 (6.59)	5.51 (5.55)
4Mi	135—137	44.55(45.42)	6.09 (6.29)	5.07 (5.30)
5Aa[a]	g)	29.87(29.39)	7.31 (7.40)	13.86(13.70)
5Ab[e]	<r. t.	35.40(39.21)	6.85 (7.99)	10.31(10.07)
5Ac[c]	≈r. t.	43.96(43.77)	8.63 (8.77)	11.27(11.34)
5Ad[f]	78—82	51.07(50.38)	9.75 (9.49)	9.69 (9.59)
5Ae	g)	62.23(62.25)	6.86 (6.87)	7.52 (7.64)
5Af[a]	g)	36.99(36.49)	7.18 (7.44)	12.53(12.16)
5Ba	120—123	48.02(48.34)	6.01 (6.09)	11.01(11.28)
5Bb	<r. t.	e)		
5Bc	≈r. t.	55.24(55.21)	7.67 (7.61)	9.32 (9.20)
5Bd	95—97	57.61(57.78)	8.06 (8.18)	8.23 (8.42)
5Be	124—126	67.68(67.24)	6.41 (6.35)	6.76 (6.54)
5Bf[a]	177—178	49.46(49.27)	6.27 (6.55)	9.56 (9.58)
5Ca	175—213	25.10(24.99)	4.14 (4.19)	11.61(11.66)
5Cb	g)	31.14(31.32)	5.28 (5.26)	10.48(10.44)
5Cc	93—95	36.46(36.46)	6.12 (6.12)	9.63 (9.45)
5Cd	150—153	40.63(40.71)	6.82 (6.83)	8.54 (8.63)
5Ce	129—130	54.31(54.26)	5.27 (5.27)	6.67 (6.66)
5Cf[b]	202—203	30.67(30.53)	4.71 (4.76)	10.50(10.17)
5Cm[d]	59—61	46.02(45.87)	4.37 (4.20)	7.16 (7.15)
5Da	125—127	19.34(19.23)	2.78 (2.90)	9.08 (8.97)
5Db	*ca.* 106	26.13(26.08)	3.50 (3.44)	8.86 (8.69)
5Dc	100—120	31.16(30.85)	4.32 (4.31)	8.02 (7.99)
5Dd	*ca.* 100	35.01(34.91)	5.11 (5.06)	7.42 (7.40)
5Dm	97—100 (subl)	43.23(43.05)	2.68 (2.65)	6.74 (6.69)
5Dt	164—166	46.13(45.94)	2.99 (2.95)	6.23 (6.30)
5Ed	150—152	58.75(58.91)	8.44 (8.43)	8.10 (8.09)
5Fd	g)	63.92(63.91)	7.52 (7.41)	6.85 (7.10)
5Gd	150—152	57.58(57.56)	10.67(10.52)	8.34 (7.90)
5Hm	115—125	49.90(49.98)	3.26 (3.26)	6.39 (6.48)
5Ho	g)	52.11(52.13)	3.92 (3.91)	6.10 (6.08)
5Hp	g)	51.88(52.13)	3.90 (3.91)	6.06 (6.08)
5If	g)	e)		
5Mb	g)	34.44(34.83)	6.65 (6.47)	11.74(11.60)
7Ag	*ca.* 80 (subl)	41.06(41.21)	6.07 (6.05)	3.91 (4.01)
7Be	134—136	60.61(60.51)	5.11 (5.08)	2.54 (2.61)

Table 2. (Continued)

Compd	Dec temp °C	Found(Calcd)(%) C	H	N
7Bi	148—149	58.14(58.43)	5.66(5.69)	2.80(2.73)
7Bm	120—130	59.08(59.13)	4.56(4.56)	2.91(2.76)
7Bn	130—131	60.00(59.84)	4.88(4.83)	2.80(2.68)
7Bq	166—169	58.82(58.86)	5.11(5.12)	5.13(5.08)
7Ci	127—129	36.27(36.20)	3.86(3.85)	2.83(2.81)

a) Dihydrate. b) Monohydrate. c) Hemihydrate. d) Trihydrate. e) The analysis is unsatisfactory because of instability. f) Hemietherate. g) Not determined.

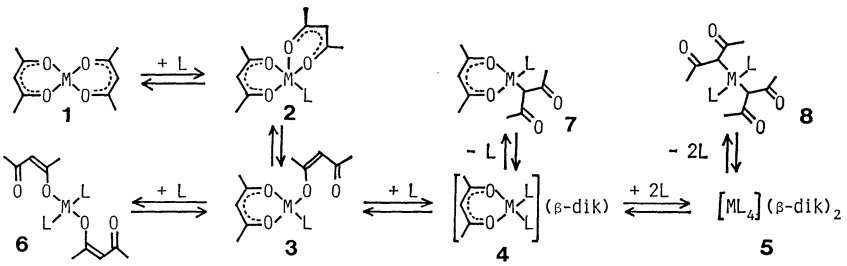


Fig. 1. The schematic sequence of reactions between the bis(β-diketonato)palladium(II) complexes and Lewis bases, L.

Table 3. Characteristic IR bands in Nujol of representative complexes

Compd	ν(NH)	ν(C=O)+ν(C=C)	Compd	ν(NH)	ν(C=O)+ν(C=C)
4Ah	3060 s	1604 vs, 1573 vs, 1543 s, 1517 vs	**5Ca**	3260 vs, 3120 s	1640 vs, 1512 s
			5Cd	3180 s, 3120 m	1638 vs, 1505 m
4Ai	3110 s	1609 vs, 1578 vs, 1525 vs, 1500 vs	**5Cm**		1635 vs, 1555 vs, 1505 s
			5Da	3340 m, 3160 s, br	1670 vs, 1590 vs, 1525 s
4Bi	3070 m	1604 vs, 1585 s, 1552 vs, 1510 vs	**5Dd**	3230 vs, 3150 s	1662 vs, 1630 s, 1524 m
			5Dt		1678 vs, 1530 vs, br
4Ci	3108 m	1636 vs, 1604 vs, 1575 m, 1524 s, 1504 m	**5Ed**	3170 vs, 3100 vs	1620 s, 1598 vs, 1560 vs, 1508 s
4Cs		1598 vs, 1542 vs, br	**5Fd**	3170 vs, 3085 vs	1601 s, 1590 vs, 1530 m, 1504 s
4Di	3170 vs	1679 vs, 1634 vs, 1604 s, 1553 vs, 1540 s	**5Gd**	3165 vs, 3100 vs	1601 vs, 1584 vs
4Ds		1681 vs, 1525 m	**5Hm**		1625 vs, 1573 s, 1506 vs
4Dt		1680 s, 1615 vs, br, 1563 vs, 1526 m, 1510 w	**5Mb**	3150 vs, br	1645 vs, 1605 vs, 1525 s, 1500 s
4Mb	3220 s, 3120 s	1649 vs, 1583 vs, 1566 vs, 1530 vs	**7Ad**	3250 s, 3180 m	1682 vs, 1640 s, 1575 vs, 1519 vs
4Mi	3110 m	1639 vs, 1602 w, 1573 s, 1546 s, 1520 s	**7Ai**	3130 w	1675 vs, 1628 w, 1570 vs, 1543 m, 1520 vs
5Aa	3180 vs, br	1609 vs, 1505 vs	**7Bi**	3130 m	1704 m, 1679 s, 1638 s, 1608 vs, 1572 s, 1523 vs
5Ad	3140 vs, 3080 s	1608 vs, 1500 vs			
5Ba	3230 vs, 3080 s	1600 vs, 1565 s, 1506 vs	**7Ci**	3150 w	1710 vs, 1660 m, 1604 vs, 1518 s
5Bd	3169 vs, 3103 s	1624 s, 1599 vs, 1572 s, 1508 s			

these cases except **4Mb**. On the other hand secondary amines can not form complexes of type **5** because of their steric requirement, but result in **4**.

Transformation of the *O,O'*-chelated 2,4-pentanedionate ligand (acac) to the central-carbon-bonded state was first found by Baba *et al.*[2] for the reactions of $[Pd(acac)_2]$ with bases in dichloromethane. The equilibrium study of the $[Pd(acac)_2]$–Et_2NH system showed that the equilibrium is almost completely shifted to **4** in methanol, but is favorable to **7** in dichloromethane.[3] Preparation of complexes **7** in the present study was therefore carried out mainly in dichloromethane.

X-Ray analysis of $[Cu(dmed)_2(hfac)_2]$ (dmed=*N,N*-dimethylethylenediamine)[12] and $[Cu(en)_2](acac)_2 \cdot 2H_2O$[13] revealed that the β-diketonate anions occupy the apical positions though the Cu–O distances (2.79 Å) are too long to be considered as the coordination bond in either case. On the contrary, the X-ray crystal structure of $[Pd(acac)(Et_2NH)_2](acac)$ (**4Ah**) determined by Kasai and his collaborators at −170 °C showed that the acac anion does not lie on the

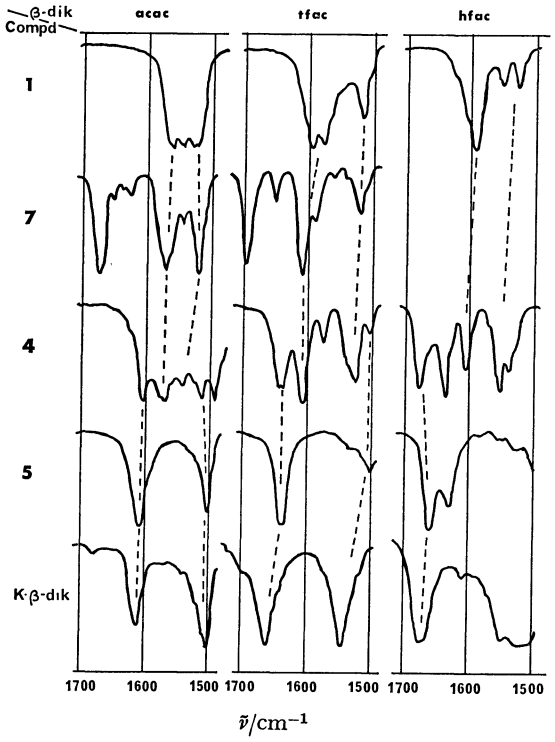


Fig. 2. IR spectra in Nujol of [Pd(β-dik)$_2$] (**1**), [Pd(β-dik)(β-dik-C^3)(pip)] (**7**), [Pd(β-dik)(pip)$_2$](β-dik) (**4**), and [Pd(PrNH$_2$)$_4$](β-dik)$_2$ (**5**) together with those of K(β-dik) hydrate for comparison.

apical position, but stands aside of the coordination plane, forming hydrogen bonds with the ligated amine groups.[14] Compound **4Ah** is not stable at room temperature even in the solid state, but looses gradually the volatile amine ligand to convert into **7Ah**.

Infrared Spectra. Characteristic IR bands of some representative mixed-ligand complexes are listed in Table 3. The bands in the 1700—1500 cm^{-1} region which are assigned to the ν(C=O)+ν(C=C) vibrations are most useful for distinguishing the bonding mode of β-diketonate anions in metal complexes. Figure 2 exemplifies these IR bands for some acac, tfac, and hfac complexes. Substitution of the methyl group in acac with the electron-attracting trifluoromethyl group raises frequency of the ν(C=O) band in each type of complexes. Thus the highest-frequency band in this region is observed at 1595 and 1591 cm^{-1} for *trans*-[Pd(tfac)$_2$] (**1C**) and [Pd(hfac)$_2$] (**1D**), respectively, 30 cm^{-1} higher than 1563 cm^{-1} for [Pd(acac)$_2$] (**1A**). The central-carbon-bonded β-diketonate ligand in **7** has the keto structure,[2] and absorbs in the 1700—1650 cm^{-1} region. The absorption bands for the β-diketonate anions in the outer sphere appear in the frequency region lower than those for the carbon-bonded β-diketonate and higher than those for the chelated one. Thus the spectra of compounds **5** are quite similar to those of K(β-dik), although the spectra of **4** are more composite since the complexes contain β-diketonate anions in both the inner and outer spheres (Fig. 2).

In crystals of [Pd(acac)(Et$_2$NH)$_2$](acac) (**4Ah**), the C–O distance of the chelated acac anion is 1.277(5) Å, nearly the same as that in [Pd(acac)$_2$] (1.275(4) Å).[14] In accordance with this situation, the ν(C=O) frequency (1573 cm^{-1}) assignable to the former carbonyl bond is not so different from that (1563 cm^{-1}) for the latter. On the other hand the ν(C=O) frequency (1604 cm^{-1}) due to the acac anion in the outer sphere conforms with the shorter C–O distance (1.246(5) Å)[14] and is close to 1610 cm^{-1} of K(acac) hydrate in which the C–O distance is 1.25(2) Å.[15]

Secondary amines coordinated to palladium(II) in complexes **4** exhibit single ν(N–H) band in the 3180—3060 cm^{-1} region, whereas primary amines in complexes **5** and **4Mb** show two bands in the 3250—3030 cm^{-1} region.

^{1}H NMR Spectra. Table 4 lists the ^{1}H NMR data for complexes **5**. In the case of the platinum(II) complexes, for instance [Pt(py)$_4$](hfac)$_2$, absence of coupling to ^{195}Pt of ^{1}H, ^{13}C, and ^{19}F atoms in hfac confirms that the hfac anions are not coordinated to the metal ion but exist in the outer sphere as counter anions.[4] The β-diketonate anions involved in **5** exhibit only one set of ^{1}H signals, indicating that the two anions in each complex are environmentally equivalent. These data do not necessarily certify that they exist in the outer sphere. However, the methyl and methine protons of [Pd(NH$_3$)$_4$](tfac)$_2$ (**5Ca**) resonate at 2.22 and 5.38 ppm from internal DSS in D$_2$O (Table 4). The chemical shifts coincide with those of K(tfac), indicating that **5Ca** dissociates completely in D$_2$O. Proton signals from the ammine ligands were not observed because of rapid H-D exchange with D$_2$O.

In spite of their salt-like structures, most of complexes **4** and **5** are not soluble in water, but dissolve in organic solvents and the β-diketonate anions seem to be associated with the cation in solution. Thus, for instance, molecular weights determined in dichloromethane at 25 °C of **4Ch**, **4Ci**, and **5Dm** are 534, 551, and 811 in fair agreement with the calculated values 559, 583, and 837, respectively. The amine protons of complexes **4** and **5** resonate generally at substantially lower field than those of the corresponding neutral complexes **7**. The amine signal from **5Ad** for instance, is shifted downfield by 2.6 ppm compared with that from **7Ad** in C$_6$D$_6$. Similarly the amine protons of **4Ag**, **4Ai**, and **4Ci** resonate at lower field in C$_6$D$_6$ by 3.2, 3.2, and 3.4 ppm than the corresponding complexes **7**, respectively. Thus the hydrogen-bonding interaction between the coordinated amine and the β-diketonate anion in the outer sphere as revealed in crystals[14] persists in solution and is stronger in the case of compounds **4** than in **5**. The sequence of chemical shift (ppm) of the propylamine protons in CDCl$_3$, **5Bd**(5.8)>**5Ad**(5.6)>**5Cd**(5.3)>**5Dd**(4.9), reflects the relative strength of hydrogen bonding by the β-diketonate anions in accordance with the basicity sequence,[16] bzac~acac>tfac>hfac.

The methyl protons of β-diketonate anions in **5** resonate at about 0.3 ppm higher field than those in the corresponding parent bis-chelates,[11] reflecting the higher charge density in the former than in the latter. Complexes **5Ae**, **5Be**, and **5Ce** exhibit the methyl proton signals at extraordinarily high field. The phenyl ring of benzylamine in these complexes may exert the anisotropic shielding effect. It is strange that

Table 4. ^{1}H NMR data for complexes **5**, $[PdL_4](\beta\text{-dik})_2$[a]

Compd	Solvent[b]	β-dik			L[c]	
		Me	Ph or *t*-Bu	CH	NH_2	Other
5Ab	i	1.76		5.00[d]	5.4[d]	Me : 2.42 t, br[6]
5Ac	i	1.67		4.97[d]	5.5[d]	Et : 2.6 br, 1.13 t(7)
	ii	1.84		5.26	5.8	Et : 2.5_5 br, 1.27 t(7)
5Ad	i	1.71		5.02[d]	5.6[d]	Pr : 2.52 br, 1.60 m, 0.86 t(7)
	ii	1.90		5.37	6.0_1	Pr : 2.67 br, 1.8 m, 0.96 t(7)
	vi	1.68		5.0	5.6_0	Pr : 2.5_6 br, 1.5 m, 0.86 t(7)
5Ae	i	1.26		4.51[d]	6.5[d]	CH_2 : 3.7_0 br, Ph : 7.3 m
5Bb	ii	2.04	7.9m, 7.1m	6.02	6.0	Me : 2.11 t, br[7]
5Bc	i	1.88	7.7m, 7.1m	5.69[d]	5.8[d]	Et : 2.5_7 br, 1.11 t(7)
	ii	2.02	7.9m, 7.1m	5.97	6.0	Et : 2.4_7 br, 1.21 t(7)
5Bd	i	1.83	7.6m, 7.2m	5.64[d]	5.8[d]	Pr : 2.5 br, 1.5 m, 0.74 t(7)
	ii	2.09	8.0m, 7.2m	6.07	6.2_2	Pr : 2.6_5 br, 1.80 m, 0.82 t(7)
5Be	i	1.38	7.1m	5.17[d]	6.5[d]	CH_2 : 3.5_5 br, Ph : 7.1 m
5Ca	viii	2.22		5.38	d)	
5Cb	i	1.90		5.36[d]	5.0_5 d[d]	Me : 2.37 t[6]
	ii	1.75		5.55	5.1_8 d	Me : 2.04 t[6]
5Cc	i	1.82		5.39	5.2	Et : 2.6 br, 1.07 t(7)
	ii	1.73		5.70	5.4	Et : 2.4 br, 1.13 t(7)
5Cd	i	1.85		5.46	5.3	Pr : 2.5_4 br, 1.47 m, 0.85 t(7)
	ii	1.77		5.75	5.5	Pr : 2.5_3 br, 1.6_7 m, 0.88 t(7)
5Ce	i	1.32		4.61	5.9	CH_2 : 3.5_7 br, Ph : 7.1 m
	ii	1.32		4.86	6.0	CH_2 : 3.5_5 br, Ph : 7.2 m
	iii	1.35		4.69	6.0	CH_2 : 4.0 br, Ph : 7.2 m
5Cm	vii	2.47		5.97		e)
5Dd	i			5.92	4.9	Pr : 2.5_3 br, 1.4_5 m, 0.8_5 t(7)
5Dm	i			6.00		py : 9.81 dd(5 and 2), ≈7.6 m, ≈7.4 m
5Ed	i	1.49		Ph : 7.1m	5.8	Pr : 2.6 br, 1.5 m, br, 0.94 t(7)
5Fd	i		7.7m, 7.1m	6.33[d]	6.0[d]	Pr : 2.5 br, 1.5 m, br, 0.63 t(7)
5Gd	i		1.00	5.33[d]	5.5[d]	Pr : 2.5 br, 1.4 br, 0.76 t(7)
5Hm	vii	thienyl protons[e]		4.70		e)
5Mb	i	1.78	-acac-	5.10	5.3	Me : 2.43 t[6]
		1.93	-tfac-	5.43		
5Mc	ii	1.82	-acac-	5.27	5.9	Et : 2.5 br, 1.20 t, br(7)
		1.75	-tfac-	5.70	5.3	

a) Chemical shifts in ppm from internal Me_4Si in various solvents except D_2O in which sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as internal referrence. b) Solvent: i) $CDCl_3$, ii) C_6D_6, iii) $(CD_3)_2CO$, iv) $(CD_3)_2SO$, v) CD_3OD, vi) CD_2Cl_2, vii) py, viii) D_2O. c) Figures in parentheses and brackets give J(CH-CH) and J(CH-NH), respectively, in Hz. The NH_2-proton signals are usually broad. d) The H-D exchange reaction occurs with the solvent. e) Indiscernible due to overlapping with other signals.

compounds **5Cd** and **5Dd** give the molecular-weight values of 1330 and 1522, respectively, in dichloromethane at 25 °C which are equal to twice the calculated values. The molecular weight of **5Ad** also exceeds the value (665) calculated for monomer, depending substantially on concentration: 720—855 for 0.01—0.1 mol(monomer) dm^{-3}. The ^{19}F NMR spectrum (one signal at 77.7 ppm upfield from $CFCl_3$ in CH_2Cl_2) and the ^{13}C NMR data of **5Dd** which will be described later indicate that the two hfac anions are magnetically equivalent as was shown by the ^{1}H NMR spectrum. The dimeric structures of these compounds are very interesting and X-ray analysis of **5Dd** is now in progress.

Compounds **5Mb** and **5Mc** which were prepared by the reactions of [Pd(acac)(tfac)] (**1M**) with methylamine and ethylamine, respectively, exhibit two sets of methyl and methine signals assignable to the acac and tfac anions in the outer sphere. It is interesting that **5Mc** shows two amine-proton signals at 5.9 and 5.3 ppm in C_6D_6, presumably distinguishing the hydrogen-bonding with acac and tfac anions, although **5Mb** gives only one NH_2 signal in $CDCl_3$.

Table 5 lists the ^{1}H NMR data for complexes **4**. In accordance with the proposed structure, compounds **4A**, **4B**, **4C**, and **4M** exhibit two sets of proton signals from both β-diketonate anions in inner and outer spheres. The signal assignment was made by reference to data for the parent bis-chelates[11] and complexes **5** (Table 4). Results obtained for the related

Table 5. ^{1}H NMR data for complexes **4**, [Pd(β-dik)L$_2$](β-dik)[a]

Compd	Solvent[b]	β-dik(IS)		β-dik(OS)		L[c]	
		CH_3	CH	CH_3	CH	NH	Other
4Ag	i	1.93	5.27[d]	1.83	5.02[d]	d)	Me : 2.40
	ii	1.51	4.87	2.05	5.38	7.7	Me : 2.31 br
	iii	2.03	5.53[d]	1.75	4.98[d]	7.4[d]	Me : 2.42 br
4Ah	i	1.98	5.38[d]	1.98	5.04[d]	7.1[d]	Et : 2.6 m, 1.53 t(7)
	ii	1.61	5.00	2.11	5.45	8.1_2	Et : 2.7 m, 1.52 t(7)
	iii	1.99	5.51	1.79	4.92[d]	7.5[d]	Et : 2.6 m, 1.49 t(7)
	iv	1.98	5.54	1.80	4.70	6.5_4	Et : *ca.* 2.5 m, 1.43 t(7)
	v	2.02	5.55[d]	2.02	d)	d)	Et : 2.6 m, 1.53 t(7)
	vi	1.96	5.39	1.88	4.92	7.2_4	Et : 2.5 m, 1.49 t(7)
4Ai	i	1.92	5.22[d]	1.83	5.03[d]	7.0[d]	pip[f] : 3.2, 2.7, 1.4_5
	ii	1.60	4.95	2.12	5.47	7.8	pip[f] : 3.7, 2.7, 1.3_7
4Bi	ii	1.75	5.68	2.21	6.12	e)	pip[f] : 3.6, 2.7_5, 1.3_7
4Cg	i	2.14	5.86	1.96	5.45	7.1[d]	Me : 2.43 d[$5._5$] and 2.40 d[$5._5$]
	ii	1.38	5.41	1.97	5.85	7.4	Me : 2.12 d[6]
	vi	2.15	5.80	1.91	5.32	6.9	Me : 2.41 d[6] and 2.37 d[6]
4Ch	i	2.13	5.78	1.99	5.40	7.1	Et : 2.5_5 m, 1.52 t($6._5$), and 1.49 t(6.5)
	ii	1.37	5.32	1.91	5.67	7.5	Et : 2.4 m, 1.35 t($6._5$)
4Ci	ii	1.42	5.42	1.99	5.89	7.4_6	pip[f] : 3.3, 2.5, 1.25
4Cj	i	2.17	5.73	2.01	5.43	7.5	Me : 1.80 d[5] and 1.72 d[5] CH_2 : 3.5—3.1 m; Ph : 7.2_6 br
	ii	1.24	5.28	1.96	5.87	8.1	Me : 1.86 d[5] and 1.74 d[5] CH_2 : *ca.* 3.3 m; Ph : 7.4 m, 7.0 m
4Ck	i	2.12	5.73	1.82	5.50	7.8	CH_2 : 3.3 m; Ph : 7.23 m, 7.13 m
	ii	1.05	5.22	2.02	5.93	8.3	CH_2 : 3.5 m; Ph : 7.3 m
4Cs	i	2.47	6.14	2.25	5.44		bpy : 8.9—7.3 m
4Di	i		6.26		5.89	6.90	pip[f] : 3.4 d, 2.8, 1.51
	ii		5.85		6.35	6.88	pip[f] : 3.1 d, 2.3_2 q, 1.1
4Dt	i		6.08 br		6.08 br		bpy : $H^{3,3'}$ 9.14 br, $H^{5,5'}$ 7.4_6 d, br(6), $H^{6,6'}$ 8.0_8(6), $Me^{4,4'}$ 2.65
4Du	iii		5.96		e)		phen : $H^{3,8}$ 8.77 d(8), $H^{4,7}$ 7.80 d(8) $H^{5,6}$ 8.05, $Me^{2,9}$ 3.04
4Mb[g]	i	1.93	5.43[d]	2.41	5.37[d]	5.3[d]	Me : 2.41 d[$6._5$] and 2.23 d[$6._5$]
4Mh[g]	i	1.96	5.35	2.07	5.31[d]	6.5_5[d]	Et : 2.6 m, 1.51 t(7)
	ii	1.55	4.85	1.95	5.67	7.1	Et : 2.5 m, 1.42 t(7)
4Mi[g]	ii	1.59	4.94	2.02	5.95	7.2	pip[f] : 3.4, 2.7, 1.3

a—e) Same as footnotes for Table 4. IS and OS abbreviate inner and outer spheres, respectively. f) Chemical shifts refer to $H^{2,6}$(equatorial), $H^{2,6}$(axial), and $H^{3,4,5}$(equatorial) in this sequence. Signals are all broad and those for $H^{3,4,5}$(axial) are indiscernible. g) The acac anion exists in IS and tfac in OS.

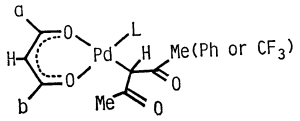
platinum(II) complexes such as [Pt(β-dik)(pip)$_2$](β-dik)[5] were also helpful. Thus the methyl and methine protons resonating at higher field in $CDCl_3$ were assigned to the β-diketonate anion in the outer sphere.

It is noticed in Table 4 that the methyl and methine resonances from the acac (**5A**) and bzac (**5B**) compounds are shifted downfield by 0.14—0.26 ppm and 0.28—0.43 ppm, respectively, in C_6D_6 as compared with those in $CDCl_3$. In the case of the tfac compounds (**5C**), the methine protons are shifted in the same direction by 0.19—0.31 ppm but the methyl protons show slight upfield shifts by 0—0.15 ppm in C_6D_6. The same trend is observed for β-diketonate anions in the outer sphere of compounds **4** (Table 5). On the contrary, the methyl and methine resonances from the chelated β-diketonate ligands are shifted upfield by 0.32—0.42 ppm and 0.27—0.40 ppm for acac (**4A**) and by 0.57—0.93 and 0.45—0.51 ppm for tfac (**4C**), respectively.

Pinnavaia and Fay[17] compared the methyl and methine chemical shifts for [M(acac)$_4$] and [M(tfac)$_4$] [M=Zr, Hf, Ce, and Th) as well as for free ligands in C_6D_6 with those in $CDCl_3$ and CCl_4. All signals were shifted upfield in C_6D_6; the methyl signals from enol tautomers of acacH and tfacH by 0.39 and 0.89 ppm, and the methine signals by 0.48 and 0.60 ppm, respectively. The metal chelates showed the same trend but the shifts were less pronounced. The authors ascribed the solvent effect to the diamagnetic anisotropy of the benzene ring and the especially large upfield shifts for the free ligands were supposed to result from a sandwiching of the planar enol molecules between the benzene molecules.

The present data are quite different from theirs, the upfield shifts for the chelated ligands being much pronounced and the effect on the counter anions being

Table 6. ^{1}H NMR data for complexes **7**[a]



Compd	Solvent[b]	[*cis*]/[*trans*]	Isomer[f]	Chelated β-dik a	Chelated β-dik b	Chelated β-dik CH	*C*-Bonded β-dik Me	*C*-Bonded β-dik CH	L[c] NH	L[c] Other
7Ab	ii			1.71	1.75	5.08	2.17	4.56	3.4	Me : 2.02 t[7]
7Ad	ii			1.72	1.75	5.09	2.19	4.57	3.4	Pr : 2.4 m, 1.4 m, 0.73 t(7)
7Ae	ii			1.73	1.73	5.08	2.11	4.55	e)	CH_2 : 3.5 br
7Ag	i			1.91	1.92	5.25[d]	2.16	4.47[d]	3.9	Me : 2.25 d[6]
	ii			1.66	1.71	4.98	2.07	4.49	4.5	Me : 2.02 d[6]
7Ah	i			1.96	1.97	5.34[d]	2.19	4.52[d]	3.4	Et : 2.6 m, 1.32 t(7)
7Ai	ii			1.75	1.75	5.06	2.10	4.59	4.6	pip[g] : 2.8—2.3, 1.2
7Ak	ii			1.67	1.81	5.06	1.81	4.32	5.1	CH_2 : 4.0 d, 3.4 d(AB quartet) Ph : 7.5 m, 7.0 m
7Be	i	1/1	*cis*	2.09	Ph	5.96	2.31	5.36	d)	CH_2 : 3.6 br
			trans	Ph	2.16	5.96	2.31	5.30		
	ii	1/1	*cis*	1.79	Ph	5.87	2.19	5.54	e)	CH_2 : 3.6 br
			trans	Ph	1.89	5.87	2.22	5.51		
7Bi	ii	6/7	*cis*	1.80	Ph	5.79	2.19	5.77	4.8	pip[g] : 3.1—2.4, 1.2
			trans	Ph	1.97	5.79	2.23	5.74		
7Bm	i	3/2	*cis*	1.99	Ph	5.97	2.47	5.00		py : 8.6_6 m, $8._0$ m
			trans	Ph	2.12	5.95	2.38	5.17		
	ii	5/3	*cis*	1.69	Ph	5.90	2.83	5.23		py : 8.72 m, 6.5 m
			trans	Ph	1.87	5.85	2.64	5.39		
7Bn	i	3/2	*cis*	1.93 1.89	Ph	5.94 5.92	2.41 2.37	5.10 4.92		Me : 2.19
			trans	Ph	2.12 2.06	5.97 5.86	2.37 2.22	5.13 5.07		Me : 2.91, 2.75 py : 8.6 m, *ca.* 7.9 m
7Bq	i	5/3	*cis*	2.00	Ph	6.00	2.54	4.98		NMe_2 : 2.10
			trans	Ph	2.10	5.96	2.44	5.10		py : 8.16 d(7), 6.49 d(7)
7**Cg**	ii	3/4	*cis*	1.39		5.30	1.87	4.80	3.7	Me : 1.73 d[6]
			trans		1.46	5.30	1.92	4.76		Me : 1.72 d[6]
7Ch	ii	1/2	*cis*	1.44		5.43	1.94	4.85	3.5	CH_2 : 2.1 m, br{CH_3 : 1.03 t(7), CH_3 : 0.99 t(7)}
			trans		1.48	5.38	1.99	4.75		
7Ci	i	3/2	*cis*	2.14		5.81	2.34	4.94	3.5_4	pip[g] : 2.78, 1.64
			trans		2.21	5.81	2.33	4.92		
	ii	3/2	*cis*	1.51		5.49	1.96	4.98	4.0_4	pip[g] : 2.6, 1.1
			trans		1.52	5.51	1.92	5.01		
7Ck	ii	1/1	*cis*	1.43		5.43	1.53	4.65	e)	CH_2 : *ca.* 3.6 m
			trans		1.43	5.39	1.54	4.52		

a—e) Same as footnotes for Table 4. f) *cis* and *trans* mean *cis*(Me, L) and *trans*(Me, L), respectively. g) Chemical shifts refer to $H^{2,6}$ and $H^{3,4,5}$, respectively. Signals are all broad.

reversed. Benzene molecules may exert the diamagnetic anisotropic effect on the chelated β-diketonate ligand by sandwiching the coordination plane. The β-diketonate anion in the outer sphere is oblique to the coordination plane, forming hydrogen bonds with amine ligands.[14] Thus the methyl and methine protons of the counter anion may experience the paramagnetic anisotropy of the benzene rings.

Since the tfac ligand is unsymmetric, two alkylamines in complexes **4C** are not environmentally equivalent. Thus two sets of the alkyl proton signals from the amine ligands are observed for **4Cg**, **4Ch**, and **4Cj**. In the reactions of [Pd(acac)(tfac)] (**1M**) with nitrogen bases, two types of products, [Pd(acac)L_2](tfac) and [Pd(tfac)L_2](acac) are conceivable. However ^{1}H NMR spectra indicate that the former type of products were obtained exclusively in each case (**4Mb**, **4Mh**, and **4Mi** in Table 5), reflecting the substantial difference in basicities of the acac and tfac anions.

Complex **4Dt** exhibits only one broad methine proton signal at 6.08 ppm in $CDCl_3$ at room temperature. The signal becomes sharper with increasing temperature probably by virtue of enhanced exchange between the two hfac anions in inner and outer spheres. The base L_2 (4,4′-Me_2-bpy) freed by reaction (1) may attack **4Dt** to give rise to **5Dt** in reaction (2).

$$[Pd(hfac)L_2](hfac) \rightleftharpoons [Pd(hfac)_2] + L_2 \quad (1)$$

$$[Pd(hfac)L_2](hfac) + L_2 \rightleftharpoons [PdL_4](hfac)_2 \quad (2)$$

Compound **5Dt** was isolated (Table 2) but its NMR spectrum is not determined because of poor solubility.

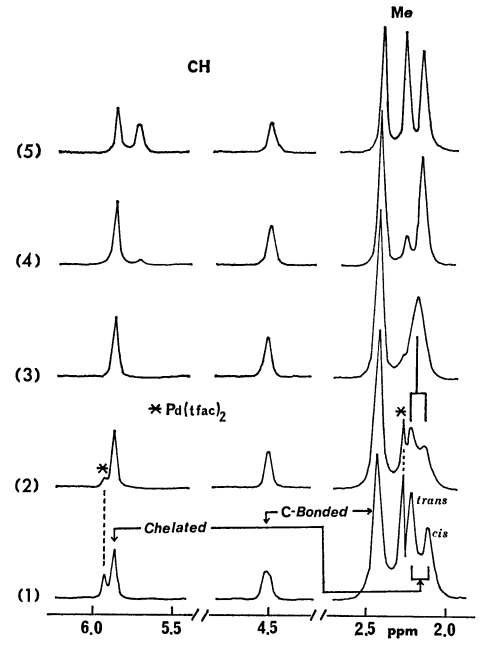


Fig. 3. ^{1}H NMR spectra of $CDCl_3$ solutions containing [Pd(tfac)$_2$] and various amounts of pyridine, the [pyridine]/[complex] molar ratio being 1.0(1), 1.5(2), 3.0(3), 6.0(4), and 11.0(5).

Averaging of the hfac anions in **4Dt** may be realized either by reaction (1) alone or by both of (1) and (2). A similar exchange of tfac anions in [Pd(tfac)(PPh$_3$)$_2$](tfac) was also noticed,[18] but the interrelation between the rate of exchange and the natures of β-diketonate and base ligands has not been studied.

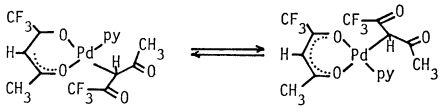
The ^{1}H NMR data for complexes **7** are collected in Table 6. Spectra in $CDCl_3$ of the acac complexes **7A** are similar to those reported for analogous complexes containing triphenylphosphine, pyridine, diethylamine, and *N*-methylbenzylamine as L[2] except that the chemical-shift difference for the two methyl groups of the chelated acac ligand is quite small in the present complexes **7**. By reference to the previous work[2] the signal at the highest field in $CDCl_3$ was assigned to the methyl group (a) located at the position cis to L and the lower-field signal to the methyl group (b) trans to L. The 6H signal around 2 ppm is easily assigned to methyl protons of the carbon-bonded acac ligand, of which the methine proton resonates at higher field than that of the chelated acac ligand.[2]

Since the bzac and tfac ligands are unsymmetric, two geometrical isomers, *cis*(Me,L) and *trans*(Me,L) are conceivable for **7B** and **7C**. In fact proton signals from these complexes exhibit splitting. The higher-field one of the two methyl signals from the chelated β-dik was assigned to the *cis*(Me,L) isomer based on the above consideration and the equilibrium quotient *cis*(Me,L)/*trans*(Me,L) was determined as the signal area ratio. Complexes **7B** except **7Bi** showed a single set of proton signals assignable to *cis*(Me,L) immediately after dissolution, but new signals ascribable to *trans*(Me,L) grew with time at the expense of the *cis*(Me,L) signals to attain an equilibrium. The rate of geometrical isomerization depends on the nature of L, **7Bm** and **7Bn** attaining equilibrium within 3 and 30 min, respectively, but **7Be** requiring *ca.* 10 h.

The [*cis*]/[*trans*] equilibrium quotient is 1 for **7Be** containing benzylamine as L and is larger than 1 for **7Bm**, **7Bn**, and **7Bq** containing pyridines, while the *trans*(Me,L) isomer is slightly more favorable for the piperidine complex, **7Bi**. In the case of **7C**, the *trans*(Me,L) isomers are favorable except for **7Ci** and **7Ck**. Complexes **7I** containing nitrogen bases as L also favor the *trans*(Me,L) form.[9]

Attainment of the isomerization equilibrium is accelerated by a free ligand L. Figure 3 shows ^{1}H NMR spectra of solutions containing [Pd(tfac)$_2$] (**1C**) and various amounts of pyridine. The spectrum in the presence of an equimolar amount of pyridine shows attainment of equilibria (3) and (4). About 80% of

$$[Pd(tfac)_2] + py \rightleftharpoons [Pd(tfac)(tfac\text{-}C^3)py] \quad (3)$$
1C **7Cm**

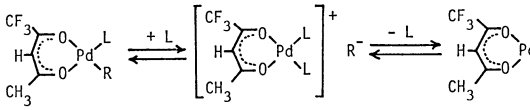


(4)

trans(Me,L)-**7Cm** *cis*(Me,L)-**7Cm**

1C is converted into **7Cm** and the *cis*(Me,L)/*trans*(Me,L) ratio is *ca.* 2/1. With increasing amount of pyridine, the methyl signals at 2.11 and 2.21 ppm become broader. When three times moles of pyridine is added, equilibrium (3) is almost completely shifted to right. The two methyl signals from the chelated tfac are also lost and instead a new signal is observed at 2.16 ppm, the chemical shift being close to the weighted mean of the values for two isomers. Thus the geometrical isomerization (exchange of the coordination sites) (Eq. 4) is assisted by free ligand and becomes fast on the NMR time scale at higher pyridine concentrations. Increased temperature also accelerates the isomerization, the *cis*- and *trans*(Me,L) signals in the presence of equimolar pyridine coalesce at higher temperatures.

Various mechanisms have been proposed for the cis-trans isomerization of square planar complexes.[19] The fact that the rapid isomerization occurs only in the presence of free pyridine does not accord with the dissociative mechanism *via* a three coordinate intermediate.[20] The double displacement mechanism[19] as is expressed by Eq. 5, where R represents the central-carbon-bonded β-diketonate ligand, is most widely accepted as the mechanism for the free-ligand catalyzed



(5)

trans(Me,L)-**7Cm** **4Cm** *cis*(Me,L)-**7Cm**

isomerization. The reactions of [Pd(acac)$_2$] with alkylamines to produce complexes **7A** were also found to proceed *via* the outer-sphere complex **4A**, the acac anion in turn replacing L as a carbanion.[3] If this mechanism is operative in the present case, that is, if the geometrical isomerization occurs rapidly on the NMR time scale *via* the forward and reverse reactions (5), environment of the carbon-bonded tfac and that

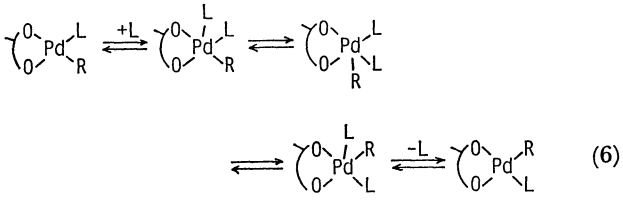
Table 7. ^{13}C NMR data for some of complexes **5**, $[PdL_4](\beta\text{-dik})_2$[a]

Compd	Solvent	β-dik						L[b]		
		CH_3	CF_3	CH	$CH_3\underline{C}O$	$CF_3\underline{C}O$	Ph$\underline{C}$O	C^α	C^β	C^γ
5Ad	CD_2Cl_2	28.8 (123)		97.7 (152)	187.5			48.3 (138)	24.8 (*ca.* 128)	11.8 (123)
	C_6D_6	29.0 (123)		98.1 (151)	187.4			48.5 (135)	24.8	11.9 (124)
5Bd	C_6D_6	29.6 (125)		96.1 (152)	189.6		183.0[c]	48.5 (136)	24.9 (129)	12.0 (127)
5Cd	$CDCl_3$	29.5 (126)	119.2 q [289]	92.8 (158)	194.6	168.2 q [30]		47.9 (137)	24.2 (128)	11.3 (126)
5Dd	$CDCl_3$		117.6 q [290]	87.6 (163)		176.0 q [33]		47.9 (139)	24.3 (125)	10.9 (127)
5Dm	$CDCl_3$		118.7 q [292]	85.2 (159)		174.4 q [30]		152.3 (188)	126.5 (170)	139.4 (167)
[K]-tfac[d]	$CDCl_3$	29.8 (126)	120.2 q [291]	92.4 (153)	194.6	168.9 q [27]				
[K]-hfac[d]	$CDCl_3$		118.3 q [291]	84.6		173.7 q [31]				

a) Chemical shifts in ppm from internal Me_4Si. Figures in parentheses and brackets give J(C-H) and J(C-F) in Hz, respectively. b) Symbols for carbon atoms are given referred to nitrogen. c) Resonances for the phenyl carbons are: quaternary C 144.7, *o*-C 127.4 (*ca.* 158), *m*-C 127.8 (*ca.* 158), and *p*-C 129.1 (159) ppm(Hz). d) [K] denotes a potassium ion surrounded by 18-crown-6, $[K(18\text{-crown-6})]^+$.

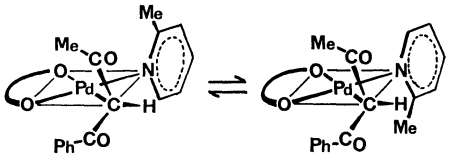
of the tfac anion in the outer sphere should be averaged. As is seen in Fig. 3, new signals grew at 2.26 and 5.69 ppm when increasing amount of pyridine was added to **7Cm**. These signals are assigned to the methyl and methine protons of the tfac anions in the outer sphere of $[Pd(py)_4](tfac)_2$ (**5Cm**). Compound **4Cm** is not so stable as to be detected spectroscopically, but converted into **5Cm**. The discrepancy in the ^{1}H chemical shifts in this reaction mixture from those (2.47 and 5.97 ppm, respectively) for pure **5Cm** in pyridine (Table 4) may be ascribed to the difference in the solution media. Thus the signals from the tfac anions both carbon bonded and in the outer sphere are separate and sharp, indicating that the exchange between these two types of tfac anions is not fast on the NMR time scale, even though the *cis*(Me,L) and *trans*(Me,L) configurations are rapidly averaged. Therefore the consecutive displacement mechanism is not realized in this case.

As an alternative mechanism for the geometrical isomerization (Eq. 4), we propose a rapid coordination site exchange of the five-coordinate square-pyramid intermediate as is exemplified in Eq. 6 by moving the unidentate ligands. Of course twisting of the chelate ring may be involved as well. This mechanism was first proposed in order to rationalize the dynamic behaviors in solution of $[M(hfac)_2P(o\text{-tolyl})_3]$ (M=Pd and Pt).[8] The exchange between apical and equatorial positions will occur *via* a trignal-bipyramid intermediate more easily than the Ray-Dutt twist in octahedral complexes.[21] Averaging of environments in solution of both halves of the 1,10-phenanthroline molecule in $[PtCN(phen)_2]NO_3$, which has a similar square-pyramid structure with a cyanide ligand in the basal plane, was also explained by virtue of an analogous mechanism.[22]



(6)

Complex **7Bn** containing 2-methylpyridine as L shows additional 1:1 splitting of each proton signal besides the splitting due to the geometrical isomerism (Table 6). This additional splitting is caused by hindered rotation of the bulky ligand around the Pd–N bond and the two sets of signals are assigned to the following two rotamers similar to those postulated for the central-carbon-bonded ester ligand in complexes **7I** containing 2-methylpyridine and 2,6-dimethylpyridine as L.[9] At higher temperatures, signals merge into one set for an equilibrium mixture of geometrical isomers.



^{13}C NMR Spectra. Table 7 lists the ^{13}C NMR data for some of complexes **5** containing propylamine or pyridine as L together with the data for [K(18-crown-6)](tfac) and [K(18-crown-6)](hfac) for comparison. The chemical shift of each carbon atom of the tfac and hfac anions involved in **5** is close to that of free anions separated from the potassium ion by virtue of the crown ether. The methyl carbons in **5** and free anions resonate at lower fields than those in the parent bis-chelates (25.4, 28.2, and 26.8 ppm for **1A**, **1B**, and **1C**), and the trifluoromethyl carbons than those in **1D** (114.7 ppm).[11] On the other hand, the methine carbons are shifted to upfield as compared with those in the corresponding bis-chelates (101.6,

TABLE 8. ^{13}C NMR DATA FOR SOME OF COMPLEXES **4**, [Pd(β-dik)L_2](β-dik)[a)]

4Ah

Solvent	acac (IS)			acac (OS)			Et_2NH	
	CH_3	CH	CO	CH_3	CH	CO	CH_2	CH_3
$CDCl_3$	26.2 (128)	100.8 (159)	186.3	28.8 br (125)	c)	188.8 br	46.5 (136)	14.2 (125)
C_6D_6	26.0 (128)	100.8 (159)	186.3	29.7 (125)	97.4 (150)	186.5	46.5 (135)	14.0 (121)

4Ci in C_6D_6

	tfac					pip[b)]		
	CH_3	CF_3	CH	CH_3CO	CF_3CO	C^α	C^β	C^γ
IS	27.5 (129)	118.1 [284]	97.3 (164)	194.1	167.4 [33]	51.1 (140)	26.5 (128)	24.1[d)] / 24.0 (128)
OS	30.1 (125)	120.6 [290]	92.5 (157)	194.7	169.2 [29]			

4Di in $CDCl_3$

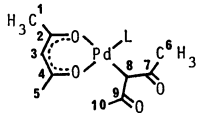
hfac (IS)			hfac (OS)			pip[b)]		
CF_3	CH	CO	CF_3	CH	CO	C^α	C^β	C^γ
116.5 [284]	92.7 (168)	175.4 [36]	118.1 [290]	86.3 (162)	175.5 [32]	51.8 (140)	26.4 (128)	23.7 (129)

4Dt in $CDCl_3$

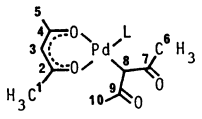
hfac			4,4′-Me_2-bpy			
CF_3	CH	CO	C^2, C^4	C^3, C^5	C^6	CH_3
117.1 [287]	88.4 br	175.0 br [34]	157.3 156.2	128.0 127.9	145.6	21.8

a, b) Same as footnotes for Table. 7. c) Indiscernible. d) Splitting due to unsymmetry of the tfac ligand.

TABLE 9. ^{13}C NMR DATA FOR COMPLEXES **7Ah**, **7Bq**, AND **7Ci** IN $CDCl_3$[a)]



cis(Me,L)



trans(Me,L)

Compd	Chelated acac			*C*-Bonded acac			L[b)]	
	C^1, C^5	C^2, C^4	C^3	C^6, C^{10}	C^7, C^9	C^8	C^α	C^β
7Ah	26.8, 27.0 (128) (128)	186.3, 186.6	100.2 (158)	31.2 (127)	202.4	48.7 (145)	46.0 (136)	14.0 (127)

Compd		Chelated β-dik[c)]					*C*-Bonded β-dik[c)]					L[b)]			
		C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^α	C^β	C^γ	NCH_3
7Bq	*cis*	27.7	188.2	97.1	178.5	137.2	31.2	206.8	44.5	196.7	140.9	150.2	107.6	154.4	39.1
	trans	27.9	187.5	97.1	179.5	138.2	31.2	206.5	44.0	196.5	140.8	150.2	107.5	154.4	39.1
7Ci	*cis*	28.2 (128)	194.6	96.2 [≈2] (164)	167.9 [33]	117.8 [284]	31.4 (128)	200.3	42.0 (147)	183.3 [33]	116.5 [293]	50.6 (141)	27.9 (132)	23.8 (128)	
	trans	28.6 (129)	194.6	96.6 [≈2] (164)	167.4 [33]	117.4 [284]	31.4 (128)	200.4	41.1 (146)	183.6 [33]	116.5 [293]	50.3 (141)	27.8 (132)	23.8 (128)	

a, b) Same as footnotes for Table 7. c) The phenyl-ring carbons except the quaternary carbon resonate in the 127.0—130.8 ppm region.

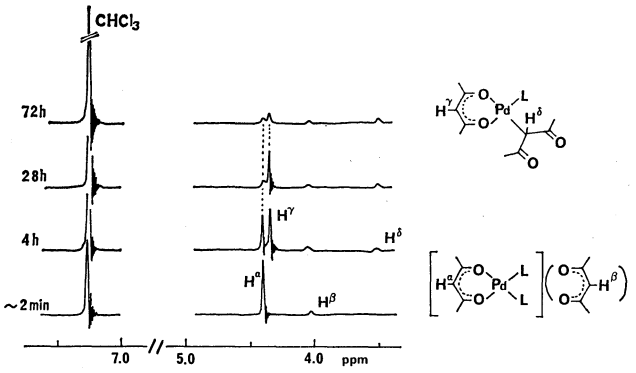


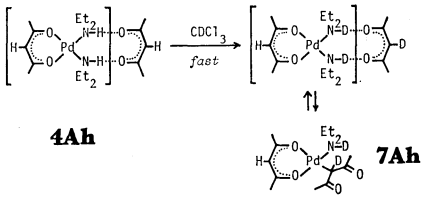
Fig. 4. Change with time of the methine proton signals from **4Ah** in $CDCl_3$ at room temperature.

98.5, 97.8, and 93.8 ppm for **1A**, **1B**, **1C**, and **1D**).[11] It should be noted that the values of ^1J(C–F) for compounds **5** and the free hfac anion (290—292 Hz) are larger and the ^2J(C–F) values (30—33 Hz) are smaller than 284 and 37 Hz, respectively, for [Pd(hfac)$_2$]. In contrast to the case of ^{1}H NMR spectra, ^{13}C resonances of β-diketonate anions in C_6D_6 make no appreciable difference from those in $CDCl_3$ and CD_2Cl_2.

Similar ^{13}C NMR data for some of compounds **4** are collected in Table 8. Each complex except **4Dt** exhibits two sets of ^{13}C signals assignable to β-diketonate anions in the inner and outer spheres. Based on the above criteria, the upfield methyl and trifluoromethyl signals and the downfield methine signal for each complex are assigned to the coordinated β-diketonate ion. It is noteworthy that the ^1J(C–H) values for methine carbons of the coordinated β-diketonate are 5—10 Hz larger than those for the anion in the outer sphere. In the case of **4Ci** and **4Di**, the ^1J(C–F) values for the tfac and hfac ions in the outer sphere are larger than those for the coordinated anions. Then the $CF_3\underline{C}O$ carbons with lower ^2J(C–F) values are ascribed to the anion in the outer sphere. Compound **4Dt** shows dynamic behavior. The environments of two hfac anions are averaged on the NMR time scale as was evidenced by the ^{1}H NMR signal for the methine proton. Both of the chemical shifts and the J(C–F) values are intermediate for those for hfac anions in inner and outer spheres. It is not certain why the ^{13}C signals from the acac anion in the outer sphere of **4Ah** are broad. Various solvents were examined but the signals were always broad except in C_6D_6.

The ^{13}C NMR spectrum of [Pd(acac)(acac-C^3)-(Et_2NH)] (**7Ah**) resembles that of [Pt(acac)(acac-C^3)-(py)] reported by Ito *et al.*[10] Spectra of **7Ah** were recorded in several solvents (Table 9) and no appreciable solvent effect is noticed. Compounds **7Bq** and **7Ci** exhibit two sets of the β-diketonate signals caused by the unsymmetry of the bzac ligand. According to the ^{1}H NMR information, a set of more intense signals was assigned to the *cis*(Me,L) isomer.

The H-D Exchange Reactions of Complexes 4 and 5 with $CDCl_3$.[23] When complexes **4A** are dissolved in $CDCl_3$, the proton signals due to NH_2 and CH of the acac anion in the outer sphere become smaller, and instead the $CHCl_3$ signal grows with time. The H-D exchange reaction attains equilibrium within several minutes in the case of **4Ag** and **4Ah**, and after about 13 min for **4Ai**. The reaction is also detected by ^{13}C NMR spectroscopy. Besides the H-D exchange, complexes **4A** change spontaneously to **7A**, attaining equilibria during several days. Figure 4 exemplifies the change with time of the methine proton signals from complex **4Ah**. The spectrum at 4 h after dissolution involves signals attributable to **7Ah**, of which the one due to the methine group of the carbon-bonded acac ligand is much weaker than the other from that of the chelated acac. This fact indicates that the carbon-bonded acac originated from the counter anion of **4Ah** in accordance with the previous kinetic evidence (Eq. 7).[3] Deuteration of the methine group



(7)

in the chelated acac anion is much slower, requiring about three days for completion. It may be accomplished by the exchange of acac anions in the inner and outer spheres as shown by Eq. 8.

$$[Pd(acac)(Et_2NH)_2](acac^*) \rightleftharpoons [Pd(acac)(acac^*)] + 2Et_2NH \rightleftharpoons [Pd(acac^*)(Et_2NH)_2](acac) \quad (8)$$

A similar reaction of **4Cg** with $CDCl_3$ is much slower, attaining equilibrium after about ten days. Transformation to **7Cg** does not occur. Because of the unsymmetric tfac chelate, two dimethylamine molecules exhibit two separate doublets at 2.40 and 2.43 ppm with $J(NH–CH_3)=5.5$ Hz (Table 5), which are transformed to singlets on deuteration of the NH proton. Amine ligands in other **4C** complexes are not deuterated by $CDCl_3$. The hfac complex **4Di** does not react either.

Complexes **5** react with $CDCl_3$ in a similar manner but the rate is slower than **4**. Necessary time for equilibrium attainment is about three days, two days, several hours, and less than 1 h for **5Ab**, **5Ac**, **5Ad**, and **5Ae**, respectively. Transformation to **7A** also occurs at the same time. Compounds **5Bd** and **5Be** attain the exchange equilibria within 16 and several hours, respectively, accompanied by the reactions to **7B**. Complex **5Cb** requires more than twenty days for completion of the reaction. Complexes **5Cc**, **5Cd**, **5Ce**, and **5Dd** are neither deuterated, nor transformed to **7**.

Amine protons and the methine proton of the tfac anion in the outer sphere of **4Mb** and **4Mh** attain the H-D exchange equilibria within several hours, but deuteration of the methine group of the chelated acac ligand requires more than four days. Substitution of the chelated acac ligand by the tfac anion *via* the pathway analogous to Eq. 8 seems more difficult than

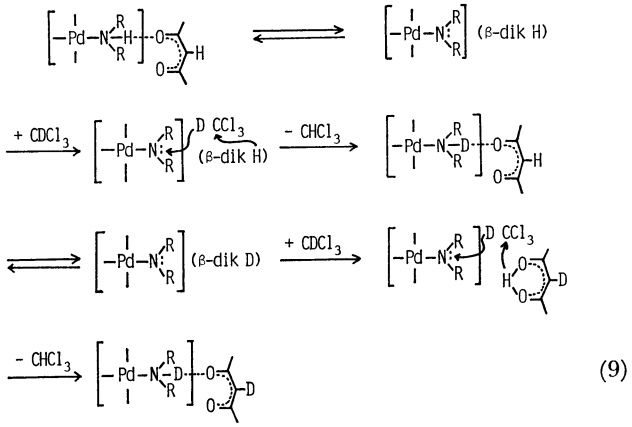
Table 10. ^{1}H NMR data for some **4C** and **5C** compounds in trifluoroacetic acid[a)]

Compd	Chelated tfac		L[b)]		tfacH	
	CH_3	CH	NH	Other	CH_3	CH
4Ch	2.26	6.14	3.7	Et : 2.8 m, 1.63 t(7), and 1.61 t(7)	2.35	6.25
4Cj	2.26	5.91	3.2	Me : 1.85 br; CH_2 : 3.6 br; Ph : 7.29	2.23	5.88
5Ca			2.90		2.27	5.98
5Ce			3.2	CH_2 : 3.51 br; Ph : 7.28	2.23	5.95
5Cf			4.13	CH_2 : 2.9 br	2.29	6.01
tfacH					2.29	6.00

a) Chemical shifts in ppm from internal DSS. b) The NH resonances are all broad. The figure in parenthesis is J(CH-CH) in Hz.

by the acac anion.

Deuteration of the coordinated amine and the β-diketonate anion in the outer sphere proceeds concurrently, and the rate seems to be greater for complexes containing stronger hydrogen bonds, since the reaction proceeds faster for **4** than for **5** and for more basic β-diketonate than for less basic anion. Kinetic study of deuteration by $CDCl_3$ of cationic palladium(II) alkylamine complexes containing various counter anions is now in progress and the following mechanism is tentatively proposed at present (Eq. 9).



(9)

Chloroform can be regarded as an acid and detritiation of C^3HCl_3 in aqueous solution by hydroxide ion[24)] and amines[25)] has been investigated. Dehalogenation of chloroform by ethylenediamine was also presumed to be initiated by proton abstraction from chloroform by the diamine.[26)] Although solutions of alkylamines in $CDCl_3$ show no sign of H-D exchange, complexes **4**, **5** or their precursors [Pd(β-dik)$_2$] can catalyze the reaction.[23)] Proton transfer from the coordinated amine to the β-diketonate anion in the outer sphere is presumed to reach equilibrium quickly and the concerted reaction among the amide center, $CDCl_3$ and β-dikH may be the rate-determining step. The deuterated amine molecule will be readily substituted by amine in solution to accomplish the catalytic cycle.

*Anion Exchange of Compounds **4** and **5**.* In order to test validity of the proposed mechanism (9) for deuteration of compounds **4** and **5** by $CDCl_3$, substitution of the β-diketonate ions in the outer sphere with other appropriate anions is desirable. As a preliminary trial some anion exchange reactions have been examined. Addition of silver nitrate to a solution of **5Cm** in pyridine resulted in [Pd(py)$_4$](NO$_3$)$_2$ in a 62% yield, and **4Ah** reacted with equimolar K(tfac) in aqueous solution to give **4Mh** in a 72% yield. Thus the β-diketonate ion in the outer sphere is easily replaced by other anions. Table 10 lists the ^{1}H NMR data for some **4C** and **5C** compounds in trifluoroacetic acid. The methyl and methine proton signals assignable to tfacH are observed, indicating that the tfac anion in the outer sphere was completely protonated by the acid. The exact chemical shifts of CH_3 and CH are more or less different from those of authentic tfacH, but the identity was confirmed in each case by addition of the authentic sample. On being left in trifluoroacetic acid for a long time, compound **5Ce** decomposed gradually to give rise to the benzylammonium ion.

Relative Stabilities in Various Bonding Modes of β-Diketonate Anions. The reactions of [Pd(β-dik)$_2$] (**1**) with excess nitrogen bases are exothermic and it depends on the natures of both the β-diketonate ligand and base employed which of compounds **4**, **5**, **7**, and **8** is produced preferentially. When the chelating ligand is the acetylacetonate or other β-diketonate of weaker basicity, primary and secondary amines afford **5** and **4**, respectively. Basicities of both types of amines are not so different and the steric requirement of secondary amines seems to make **5** unfavorable. Although 2,2′-bipyridine reacts with **1D** to afford solely **4Ds**, 4,4′-dimethyl-2,2′-bipyridine produces either of **4Dt** and **5Dt** depending on the mole ratio of the reactants. Increased basicity of the latter ligand might overcome the steric disadvantage of the bis(bpy)-complexes **5**.

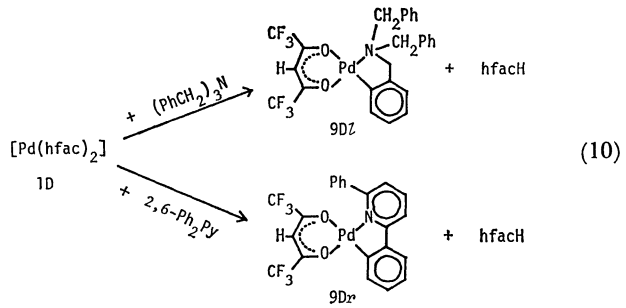
Tertiary amines do not react with **1** probably because their bulkiness is both kinetically and thermodynamically unfavorable for the ligand substitution. Tribenzylamine did react with **1D** not to afford a ligand-substituted product but to produce an orthometallated complex **9D*l***. 2,6-Diphenylpyridine also gave a similar product **9Dr**. The ^{1}H and ^{13}C NMR assay revealed that the hfac anion worked as a proton acceptor to result in hfacH (Eq. 10). In recent years a great many articles have appeared concerning orthometallated compounds, or "organometallic intramolecular-coordination compounds."[27)] Thus the reaction of lithium tetrachloropalladate(II) with *N*,*N*-dimethylbenzylamine in methanol gave di-μ-chlorobis-

Table 11. Equilibrium constants[a] estimated by ^{1}H NMR spectroscopy in $CDCl_3$ and C_6D_6 at room temperature:

4 $\rightleftharpoons$ **7** + L, $K_1 = [7]^2/[4]$; **5** $\rightleftharpoons$ **7** + 3L, $K_2 = [7]^4/[5]$

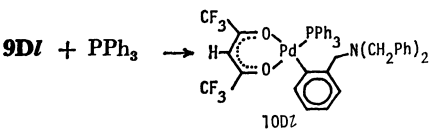
L	β-dik			
	acac	bzac	tfac	hfac
		K_1		
Me_2NH	>4 (2.6)		≈0 (1×10^{-2})	
Et_2NH	2.4 (≈0)		≈0 (≈0)	
pip	3.2 (0.2)	(3×10^{-2})	≈0 (≈0)	≈0
		K_2[b]		
$MeNH_2$	2×10^{-3}	($\ll2\times10^{-6}$)	$<2\times10^{-6}$ ($\ll7\times10^{-7}$)	
$EtNH_2$	2×10^{-3} (9×10^{-7})	6×10^{-6} ($\ll8\times10^{-7}$)	≈0 (≈0)	
n-$PrNH_2$	(1×10^{-8})		≈0 (≈0)	≈0 (≈0)
$BzNH_2$	1×10^{-2}		(2×10^{-6})	
py			$\gg8\times10^{-2}$	≈0

a) The figures in parentheses were determined in C_6D_6. The lower- and upper-limit values accompanied by the mark $\gg$ and $\ll$ were estimated by assuming concentration of the minor component as 1/10 of the initial concentration employed when it is detected but can not be determined quantitatively. The symbol ≈0 means that compound **7** can not be observed on the spectrum. b) The values of K_2 were tentatively calculated on the assumption that **5** exists as a monomer, although complexes of propylamine and presumably other alkylamines are dimeric in dichloromethane.



(10)

(*N*,*N*-dimethylbenzylamine-2*C*,*N*)dipalladium(II),[28] of which the bridge bond was cleaved by thallium(I) acetylacetonate to result in acetylacetonato(*N*,*N*-dimethylbenzylamine-2*C*,*N*)palladium(II)[29] analogous to **9D***l*. 2-Phenylpyridine also reacts with sodium tetrachloropalladate(II) to yield the chloro-bridged five-membered (*C*, *N*) chelate.[30] However, the reaction of [Pd(β-dik)$_2$] with a tertiary amine or a substituted pyridine to afford an orthometallated compound as expressed by Eq. 10 may be the first example. Furthermore it should be noted that triphenylphosphine can cleave the Pd–N coordination linkage in **9D***l* to result in a phenylpalladium(II) complex **10D***l* stable enough to be isolated (Eq. 11).



(11)

When a base reacts with complexes **1**, the β-diketonate ligand of weaker basicity is displaced more easily and the hfac and tfac ligands like to remove into the outer sphere. The acac ligand is also expelled from the coordination sphere by nitrogen bases, but the nature of solvent plays an important role in determining the most stable bonding mode. In polar solvents such as methanol compounds of type **4** and **5** are favorable, but dichloromethane stabilizes the carbon-bonded complexes.[3] The anion of ethyl acetoacetate is more basic than acac and complex **1I** readily reacts with pyridine to afford **8Im**,[9] while **1A** gives only **7Am** (Fig. 1). Thus the preference of bonding modes by β-dicarbonyl anions is related with the sequence of basicity as follows.

etac > acac ~ bzac > tfac > hfac

C-bonded——*O*,*O*′-chelate——Outer sphere

The relative tendency of β-dicarbonyl anions to form the central carbon bonding parallels with preference of the keto tautomer to enol. The percentage of enol in neat liquid at 33 °C was recorded as 8, 81, 97, and 100% for etacH, acacH, tfacH, and hfacH, respectively.[31] A β-dicarbonyl anion which prefers to accept a hydrogen ion at the central carbon atom rather than at an oxygen atom likes also to react with a metal ion as a carbanion. Ito and Yamamoto studied the reactions of [M(acac)(acac-*C*^{3})PPh_3] with several β-dikH and found that the keto-favoring β-dikH selectively replaces the carbon-bonded acac, while the enol-favoring β-dikH substitutes the chelated acac.[32]

Complexes **4**, **5**, and **8** gradually liberate base to produce **7**. Table 11 lists the equilibrium constants estimated by the ^{1}H NMR spectroscopy and supports the above conclusion concerning the preference of bonding modes. Thus the stability of the outer-sphere complexes is in the sequence of hfac>tfac>bzac>acac and RNH_2>$BzNH_2$>py. The value (2.4) of K_1 for [Pd(acac)(Et_2NH)$_2$](acac) (**4Ah**) $\rightleftarrows$ **7Ah** + Et_2NH is not so different from the more accurate value (4.46) determined in dichloromethane at 25 °C by the spectrophotometric method.[3] When compounds **5** are converted to **7**, the reaction should proceed *via* **4**. However complexes **4** containing primary amines as L are usually unstable except **4Mb** and are not detected spectroscopically. Compound **4Mb**

as well as **4Mh** and **4Mi** is very stable in solution, showing no sign of transformation to **7**. The chelate-favoring acac and the outer sphere-favoring tfac may cooperate in stabilizing these compounds.

Experimental

Preparation of Compounds. The starting complexes, bis(β-diketonato)palladium(II) [Pd(β-dik)$_2$] (**1**) including [Pd(acac)(tfac)] (**1 M**), were prepared by the methods described in a previous paper.[11] Methylamine, ethylamine, and dimethylamine were evolved by dissolving potassium or sodium hydroxide in aqueous solutions of these amines which are commercially available. Other amines, pyridines, and ammonia were purchased and used without purification. Most of the new compounds reported in this paper were prepared by one of the following two methods and the remaining compounds by other methods. (1) When the base is liquid at room temperature, compound **1** was dissolved or suspended in the neat liquid and the mixture was stirred. After reaction for appropriate time duration, the product was precipitated by cooling the solution, by adding another solvent such as diethyl ether, hexane, and petroleum ether to the reaction mixture, or by distilling away the excess base. (2) An appropriate amount of base was added to a solution of **1** in dichloromethane, benzene, or diethyl ether. The reaction mixture was worked up in a similar manner as above.

*[Pd(acac)(Me$_2$NH)$_2$](acac)·2H$_2$O (**4Ag**)*: Dimethylamine was distilled under nitrogen into a flask containing fine powder of [Pd(acac)$_2$] (**1A**) which was cooled with Dry Ice–methanol. The reaction mixture was then warmed to room temperature and stirred to result in a yellow solution. The amine was distilled away under reduced pressure to leave tiny yellow plates in a 90% yield.

*[Pd(acac)(Et$_2$NH)$_2$](acac) (**4Ah**)*: Pulverized **1A** (1.55 g, 5.09 mmol) was added to diethylamine (*ca.* 10 cm^3) and the mixture was warmed to result in a yellow solution, which was then cooled and kept at −5 °C in a refrigerator overnight to precipitate yellow columns. The product was filtered and washed several times with petroleum ether (boiling point<60 °C). The yield was 1.52 g (66%).

*[Pd(acac)(pip)$_2$](acac)·H$_2$O (**4Ai**)*: Complex **1A** (215 mg, 0.706 mmol) was dissolved in piperidine (*ca.* 0.8 cm^3) and diethyl ether (*ca.* 30 cm^3) was added to the solution. The solvent was then allowed to evaporate spontaneously to leave yellow needles on the wall of vessel. The product was gathered and washed with hexane. The yield was 156 mg (45%).

*[Pd(bzac)(pip)$_2$](bzac) (**4Bi**)*: Hexane was added to a solution of [Pd(bzac)$_2$] (**1B**, 59 mg, 0.14 mmol) in piperidine (0.9 cm^3) and the mixture was kept in a refrigerator to deposit yellow needles. The product was filtered and washed with a mixture of diethyl ether and petroleum ether (1:1 by volume). The yield was 77 mg (93%).

*[Pd(tfac)(Me$_2$NH)$_2$](tfac) (**4Cg**)*: In a similar manner as for **4Ag**, [Pd(tfac)$_2$] (**1C**, 300 mg, 0.727 mmol) was dissolved in dimethylamine. The amine was then distilled away to leave a yellow powder (331 mg) in a 91% yield.

*[Pd(tfac)(Et$_2$NH)$_2$](tfac) (**4Ch**)*: After **1C** (200 mg, 0.484 mmol) was dissolved in diethylamine, the excess amine was distilled away promptly under reduced pressure to leave a yellow crystalline solid (238 mg) in an 88% yield.

*[Pd(tfac)(pip)$_2$](tfac) (**4Ci**)*: Piperidine (*ca.* 0.2 cm^3) was added dropwise to a suspension of **1C** (413 mg, 1.00 mmol) in dichloromethane (0.5 cm^3) with stirring to result in a yellow solution. Hexane (20 cm^3) was added and the mixture was kept in a refrigerator overnight to deposit pale yellow plates (252 mg). The filtrate was concentrated and then cooled to precipitate another crop. The total yield was 392 mg (67%).

*[Pd(tfac)(BzNHMe)$_2$](tfac) (**4Cj**)*: A dichloromethane solution (2 cm^3) of *N*-methylbenzylamine (214 mg, 1.77 mmol) was added slowly to a solution of **1C** (511 mg, 1.24 mmol) in dichloromethane (5 cm^3) with stirring. After further addition of the amine (200 mg, 1.65 mmol), the solvent was allowed to evaporate spontaneously. Yellow crystals deposited on the wall of vessel were collected and washed with a mixture of diethyl ether and petroleum ether (1:1 by volume). The yield was 581 mg (72%).

*[Pd(tfac)(Bz$_2$NH)$_2$](tfac) (**4Ck**)*: Complex **1C** (100 mg, 0.242 mmol) was dissolved in hot dibenzylamine. Hexane was added to the solution to deposit a yellow precipitate, which was filtered and washed with hexane. The yield was 132 mg (67%).

*[Pd(tfac)(bpy)](tfac) (**4Cs**)*: A benzene solution (2 cm^3) of 2,2′-bipyridine (156 mg, 1.00 mmol) was added to a solution of **1C** (413 mg, 1.00 mmol) in benzene (10 cm^3) to precipitate a yellow crystalline solid immediately, which was filtered and washed with a mixture of benzene and hexane (1:1 by volume). The yield was 489 mg (86%).

*[Pd(hfac)(Me$_2$NH)$_2$](hfac) (**4Dg**)*: In a similar manner as the case of **4Ag**, [Pd(hfac)$_2$] (**1D**, 104 mg, 0.20 mmol) was dissolved in dimethylamine. On distilling away of the amine, white cubes and red oil were left, which were extracted with diethyl ether. The solvent was allowed to evaporate spontaneously to leave yellow plates of **4Dg** and a small amount of white columns. The yield of **4Dg** was 60 mg (49%). The latter was confirmed to be dimethylammonium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate. Found: C, 33.02; H, 3.58; N, 5.54%. Calcd for C$_7$H$_9$NO$_2$F$_6$: C, 33.21; H, 3.58; N, 5.53%. IR: ν(NH) 3150s, ν(C=O) 1680vs.

*[Pd(hfac)(pip)$_2$](hfac) (**4Di**)*: Piperidine (98 mg, 1.2 mmol) was added to a solution of **1D** (300 mg, 0.576 mmol) in diethyl ether (3 cm^3). The solvent was allowed to evaporate spontaneously to leave yellow cubes in a 97% yield (387 mg).

*[Pd(hfac)(bpy)](hfac) (**4Ds**)*: A solution of 2,2′-bipyridine (71 mg, 0.45 mmol) in diethyl ether (1 cm^3) was added to a solution of **1D** (103 mg, 0.198 mmol) in diethyl ether (1 cm^3) to deposit a pale yellow precipitate immediately, which was filtered and washed with diethyl ether. The yield was 124 mg (93%).

*[Pd(hfac)(4,4′-Me$_2$-bpy)](hfac) (**4Dt**)*: In a similar manner as above, **1D** (208 mg, 0.400 mmol) reacted with 4,4′-dimethyl-2,2′-bipyridine (74 mg, 0.47 mmol) in diethyl ether (2 cm^3) to precipitate yellow needles immediately. The yield was 259 mg (92%).

*[Pd(hfac)(2,9-Me$_2$-phen)](hfac) (**4Du**)*: White crystals of compound **4Du** were prepared in a similar way as above. The yield was about 30%.

*[Pd(acac)(MeNH$_2$)$_2$](tfac) (**4Mb**)*: Methylamine (19 mg, 0.61 mmol) was kept in a small glass-stoppered bottle cooled with dry ice-methanol. Dichloromethane (1 cm^3) was poured into this bottle quickly and the solution was added to a dichloromethane solution (1 cm^3) of **1M** (114 mg, 0.318 mmol). The mixture was kept at room temperature for 1 h. Then petroleum ether (1 cm^3) was added to the solution and solvents were allowed to evaporate spontaneously to leave yellow plates (76 mg) in a 57% yield.

*[Pd(acac)(Et$_2$NH)$_2$](tfac) (**4Mh**)*: Compound **4Mh** was prepared *via* three alternative routes. (1) Immediately after dissolution of [Pd(acac)(tfac)] (**1M**, 100 mg, 0.279

mmol) in diethylamine (2 cm³), excess amine was distilled away at room temperature under reduced pressure to leave a yellow powder (136 mg) in a 97% yield. Recrystallization from dichloromethane–hexane gave yellow plates (yield: 80 mg, 57%). (2) Aqueous solution of potassium 1,1,1-trifluoro-2,4-pentanedionate (16 mg, *ca.* 0.1 mmol) was added to a fresh solution of [Pd(acac)(Et_2NH)$_2$](acac) (**4Ah**, 44 mg, 0.098 mmol) in water (1 cm³) with stirring to separate out a yellow precipitate (36 mg) in a 72% yield. After being dried *in vacuo*, the crude product was recrystallized from dichloromethane–hexane to give yellow hexagonal plates. The yield was 25 mg (51%). (3) A methanol solution of equimolar amount of potassium 2,4-pentanedionate was added to an acetone solution of [Pd(tfac)-(Et_2NH)$_2$](tfac) (**4Ch**) and the mixture was stirred for *ca.* 10 min. The solvents were distilled away under reduced pressure and the residue was extracted with diethyl ether. Then the solvent was allowed to evaporate spontaneously to leave yellow needles of **4Mh**, but the yield was very low.

*[Pd(acac)(pip)$_2$](tfac) (**4Mi**)*: Small portions of hexane and diethyl ether were added to a solution of **1M** (100 mg, 0.279 mmol) in piperidine (0.1 cm³) and the mixture was cooled to precipitate yellow plates, which were filtered and washed with hexane. The yield was 52 mg (35%).

*[Pd(NH_3)$_4$](acac)$_2$·2H_2O (**5Aa**)*: Gaseous ammonia from a cylinder was bubbled into a solution of **1A** (254 mg, 0.834 mmol) in dichloromethane (10 cm³) for *ca.* 15 min to deposit white crystallites, which were filtered, washed with diethyl ether. The yield was 280 mg (83%).

*[Pd($MeNH_2$)$_4$](acac)$_2$ (**5Ab**)*: A suspension of **1A** (270 mg, 0.886 mmol) in several cm³ of methylamine was stirred to produce a white precipitate on reaction. After distillation of the amine, a white powder was washed with a small portion of hexane. The yield was 357 mg (94%). Compound **5Ab** is not stable but turns yellow gradually on decomposition at room temperature.

*[Pd($EtNH_2$)$_4$](acac)$_2$·1/2H_2O (**5Ac**)*: On addition of **1A** (232 mg, 0.762 mmol) to *ca.* 3 cm³ of ethylamine, a white precipitate appeared immediately. The excess amine was distilled away slowly at −5 °C to leave a pale yellow crystalline solid, which was washed with hexane. The yield was 360 mg (96%). Compound **5Ac** was alternatively obtained by addition of an aqueous solution of ethylamine drop by drop to a suspension of **1A** in acetone. It is more stable than **5Ab** but decomposes slowly at room temperature.

*[Pd($PrNH_2$)$_4$](acac)$_2$ (**5Ad**)*: When **1A** was added to propylamine with stirring, the reaction occurred exothermically to deposit a white precipitate. The excess amine was distilled away and the residue was washed with diethyl ether. The yield was quantitative and recrystallization from diethyl ether–hexane gave colorless transparent columns. Compound **5Ad** also decomposes slowly at room temperature.

*[Pd($BzNH_2$)$_4$](acac)$_2$ (**5Ae**)*: Benzylamine (1.6 cm³) was added drop by drop to a solution of **1A** (400 mg, 1.31 mmol) in dichloromethane (5 cm³) and the solution was stirred for a while. Petroleum ether (6 cm³) was added to it and the mixture was kept in a refrigerator for three days to deposit white plates (840 mg) in an 87% yield, which decompose slowly to a white powder at room temperature.

*[Pd(en)$_2$](acac)$_2$·2H_2O (**5Af**)*: Six times as many moles of ethylenediamine was added dropwise to a solution of **1A** (294 mg, 0.97 mmol) in dichloromethane (10 cm³) with stirring to deposit a white precipitate (414 mg) in a 93% yield. The method is similar to that used for preparation of [Cu(en)$_2$](acac)$_2$·2H_2O.[13]

*[Pd(NH_3)$_4$](bzac)$_2$ (**5Ba**)*: Gaseous ammonia was passed through a solution of [Pd(bzac)$_2$] (**1B**, 155 mg, 0.362 mmol) in dichloromethane at 0 °C for 10 min to separate out a yellowish white precipitate. On washing with diethyl ether a white powder of **5Ba** (164 mg) was obtained in a 91% yield.

*[Pd($MeNH_2$)$_4$](bzac)$_2$ (**5Bb**), [Pd($EtNH_2$)$_4$](bzac)$_2$ (**5Bc**), and [Pd($PrNH_2$)$_4$](bzac)$_2$ (**5Bd**)*: These compounds were obtained in similar manners as for the corresponding 2,4-pentanedionates in 90, 97, and 89% yields, respectively. Each complex decomposes gradually at room temperature.

*[Pd($BzNH_2$)$_4$](bzac)$_2$ (**5Be**)*: Cold benzylamine was added dropwise onto a fine powder of **1B** (327 mg, 0.763 mmol) with stirring at 0 °C to produce a white precipitate immediately, which was filtered and washed with hexane. The yield was 587 mg (90%).

*[Pd(en)$_2$](bzac)$_2$·2H_2O (**5Bf**)*: Five drops of ethylenediamine was added to a solution of **1B** (112 mg, 0.261 mmol) in dichloromethane to deposit a white precipitate immediately, which was filtered and washed with diethyl ether. The yield was 123 mg (81%).

*[Pd(NH_3)$_4$](tfac)$_2$ (**5Ca**), [Pd($MeNH_2$)$_4$](tfac)$_2$ (**5Cb**), [Pd($EtNH_2$)$_4$](tfac)$_2$ (**5Cc**), [Pd($PrNH_2$)$_4$](tfac)$_2$ (**5Cd**), [Pd-($BzNH_2$)$_4$](tfac)$_2$ (**5Ce**), and [Pd(en)$_2$](tfac)$_2$ (**5Cf**)*: These compounds were prepared by similar methods as those for the corresponding 2,4-pentanedionates in 90—99% yields. Recrystallization of **5Cf** from water gave colorless transparent needles of monohydrate.

*[Pd(py)$_4$](tfac)$_2$·3H_2O (**5Cm**)*: Compound **1C** (100 mg, 0.242 mmol) was dissolved in pyridine (*ca.* 0.3 cm³) and the mixture was allowed to stand overnight at room temperature. Large colorless plates were separated and washed with hexane. The yield was 144 mg (76%).

*[Pd(NH_3)$_4$](hfac)$_2$ (**5Da**):, [Pd($MeNH_2$)$_4$](hfac)$_2$ (**5Db**), [Pd($EtNH_2$)$_4$](hfac)$_2$ (**5Dc**), and [Pd($PrNH_2$)$_4$](hfac)$_2$ (**5Dd**)*: These compounds were obtained in similar manners as for the corresponding 2,4-pentanedionates in 90—99% yields. Compounds **5Db**—**5Dd** were able to be recrystallized from dichloromethane–hexane.

*[Pd(py)$_4$](hfac)$_2$ (**5Dm**)*: Compound **1D** dissolved in a small amount of pyridine exothermically. Diethyl ether and hexane were added to the solution and the mixture was cooled to deposit colorless plates in an 80% yield.

*[Pd(4,4′-Me_2-bpy)$_2$](hfac)$_2$ (**5Dt**)*: Compound **1D** (208 mg, 0.400 mmol) reacted with 4,4′-dimethyl-2,2′-bipyridine (147 mg, 0.800 mmol) in diethyl ether (4 cm³). Yellow crystallites were filtered and washed with diethyl ether. The yield was 332 mg (93%).

*[Pd($PrNH_2$)$_4$](Ph-acac)$_2$ (**5Ed**), [Pd($PrNH_2$)$_4$](dbm)$_2$ (**5Fd**), and [Pd($PrNH_2$)$_4$](dpm)$_2$ (**5Gd**)*: These compounds were obtained in 35—50% yields by dissolving [Pd(Ph-acac)$_2$] (**1E**), [Pd(dbm)$_2$] (**1F**), and [Pd(dpm)$_2$] (**1G**), respectively, in propylamine and distilling away the excess amine at −5 °C. Each product was washed with hexane.

*[Pd(py)$_4$](tta)$_2$ (**5Hm**)*: [Pd(tta)$_2$] (**1H**, 250 mg, 0.455 mmol) was dissolved in a mixture of dichloromethane (3 cm³) and pyridine (2 cm³) by stirring at 50 °C. The resulting clear solution was kept in a refrigerator overnight to give light yellow crystals, which were recrystallized from dichloromethane–petroleum ether. The yield was 350 mg (90%).

*[Pd(3-Me-py)$_4$](tta)$_2$ (**5Ho**) and* [Pd(4-Me-py)$_4$](tta)$_2$ *(**5Hp**)*: Both compounds were obtained in a similar manner as above in more than 90% yields.

*[Pd(en)$_2$](etac)$_2$ (**5If**)*: Ethylenediamine (0.5 cm³) was mixed with pulverized [Pd(etac)$_2$]·1/2H_2O[9] (277 mg, 0.741 mmol). A white precipitate deposited immediately, which was washed with large volumes of diethyl ether and acetone,

successively, and dried *in vacuo*. A gray powder of **5If** (311 mg) was obtained in an 86% yield. The compound does not dissolve in organic solvents other than alcohols, but is readily soluble in water and methanol and the ester anion in the outer sphere is solvolyzed. Thus recrystallization from a mixture of methanol, diethyl ether, and petroleum ether (2:2:1 by volume) resulted in colorless crystals of [Pd(en)$_2$](meac)$_2$·H$_2$O, where meac stands for the anion of methyl acetoacetate. Found: C, 35.99; H, 6.70; N: 11.96%. Calcd for $C_{14}H_{32}N_4O_7Pd$: C, 35.41; H, 6.79; N, 11.80%.

[Pd(MeNH$_2$)$_4$](acac)(tfac) (**5Mb**): Compound **1M** (100 mg, 0.279 mmol) was dissolved in several cm^3 of methylamine to result in a colorless solution. The excess amine was distilled away to leave white crystals (130 mg) in a 96% yield.

[Pd(EtNH$_2$)$_4$](acac)(tfac) (**5Mc**): In a similar manner as above white needles of **5Mc** were obtained in a quantitative yield. Recrystallization from petroleum ether gave pale yellow columns.

Dimethylamine(2,4-pentanedionato)(2,4-pentanedionato-C^3)palladium(II), *[Pd(acac)(acac-C^3)(Me$_2$NH)]* (**7Ag**): Compound **1A** (121 mg, 0.397 mmol) reacted with slightly excess dimethylamine (23 mg, 0.51 mmol) in dichloromethane (1 cm^3). Spontaneous evaporation of the solvent left a yellow mass and yellow liquid, which were washed with hexane to afford a yellow powder of **7Ag** (131 mg) in a 94% yield.

[Pd(acac)(acac-C^3)(Et$_2$NH)] (**7Ah**): This compound was previously prepared by the reaction of **1A** with diethylamine,[2] and now derived from **4Ah** (60 mg) by leaving its aqueous solution at room temperature. Yellow needles precipitated were filtered and dried *in vacuo*. The yield of **7Ah** from **4Ah** was 61% (31 mg).

[Pd(acac)(acac-C^3)(pip)] (**7Ai**): The compound was obtained in an 81% yield in a similar manner as **7Ag**, and recrystallized from diethyl ether–hexane. Compounds **7Ab**, **7Ad**, **7Ae**, and **7Ak** were also prepared in a similar manner.

Benzylamine(1-phenyl-1,3-butanedionato)(1-phenyl-1,3-butanedionato-C^2)palladium(II), *[Pd(bzac)(bzac-C^2)(BzNH$_2$)]* (**7Be**): Compound **1B** (179 mg, 0.418 mmol) reacted with benzylamine (71 mg, 0.66 mmol) in dichloromethane (3 cm^3) and the solvent was evaporated spontaneously to leave a yellow crystalline solid contaminated with oil. The product was washed with diethyl ether and dried *in vacuo*. The yield of a yellow powder of **7Be** was 196 mg (88%). The product was a mixture of *cis*(Me,L) and *trans*(Me,L) isomers. When it was dissolved in dichloromethane and the solvent was evaporated spontaneously after addition of a small amount of methyl iodide, a yellow crystalline solid left and washed with diethyl ether was pure *cis*(Me,L). The role of methyl iodide is not clear which was used in order to examine the possibility of substituting the carbon-bonded ligand.

[Pd(bzac)(bzac-C^2)(pip)] (**7Bi**): After the reaction of **1B** (123 mg, 0.287 mmol) with benzylamine (37 mg, 0.44 mmol) in dichloromethane (2 cm^3), the solvent was allowed to evaporate spontaneously to leave orange oil. A mixture (2 cm^3) of diethyl ether and hexane (1:2 by volume) was added to the vessel and the mixture was stirred. A yellow precipitate appeared, which was filtered, washed with diethyl ether and dried *in vacuo*. The yield was 92 mg (63%).

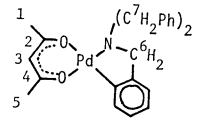
[Pd(bzac)(bzac-C^2)(py)] (**7Bm**): Compound **1B** (200 mg, 0.467 mmol) was dissolved in a small amount of pyridine by heating. Hexane was added to the solution and the mixture was cooled to deposit yellow crystals, which were filtered and washed with hexane. Compound **7Bm** (225 mg) thus obtained in a 95% yield is composed of the *cis*-(Me,L) isomer alone.

[Pd(bzac)(bzac-C^2)(2-Me-py)] (**7Bn**): Complex **7Bm** (100 mg, 0.196 mmol) was dissolved in a small amount of 2-methylpyridine by heating. Hexane was added to the solution and the mixture was cooled to separate out yellow needles (86 mg) in an 84% yield, which contain only the *cis*(Me,L) isomer.

[Pd(bzac)(bzac-C^2)(4-Me$_2$N-py)] (**7Bq**): Compound **1B** (100 mg, 0.233 mmol) reacted with 4-dimethylaminopyridine (28 mg, 0.23 mmol) in dichloromethane (2 cm^3) at room temperature. After 3 h, hexane (1 cm^3) was added to the solution and the mixture was cooled to deposit yellow needles (105 mg) in an 82% yield.

[Pd(tfac)(tfac-C^3)(Me$_2$NH)] (**7Cg**): Complex **1C** (268 mg, 0.650 mmol) reacted with twice molar dimethylamine (67 mg) in dichloromethane and the solvent was vaporized spontaneously to leave yellow plates, which were filtered and washed with hexane. The yield was 279 mg (94%). *[Pd(tfac)(tfac-C^3)(Et$_2$NH)]* (**7Ch**), *[Pd(tfac)(tfac-C^3)(pip)]* (**7Ci**), and *[Pd(tfac)(tfac-C^3)(Bz$_2$NH)]* (**7Ck**) were similarly obtained as a yellow powder, yellow needles, and yellow crystallites in 50, 80, and 50% yields, respectively.

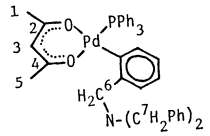
1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato(tribenzylamine-2C,N)-palladium(II), *[Pd(hfac)(Bz$_3$N-2C,N)]* (**9Dl**): A mixture of **1D** (287 mg, 0.551 mmol) and tribenzylamine (316 mg, 1.10 mmol) were heated in toluene under reflux and the solvent was distilled away under reduced pressure to leave pale yellow needles. Recrystallization from dichloromethane–petroleum ether (1:1 by volume) gave **9Dl** (196 mg) in a 52% yield. Found: C, 51.98; H, 3.45; N, 2.37%; mol wt 574 in CH_2Cl_2. Calcd for $C_{26}H_{21}NO_2F_6Pd$: C, 52.06; H, 3.53; N, 2.34%; mol wt 600. Dec temp: 152—162 °C. IR in Nujol: ν(C=O)+ν(C=C), 1640vs, 1547s, 1515m cm^{-1}. ^{1}H NMR in $CDCl_3$, δ (ppm from internal Me_4Si): 3.97 (2H, s, 6CH$_2$); 3.9 and 4.3 (4H, AB-quartet, J=12 Hz,



7CH$_2$); 5.94 (1H, s, 3CH); 7.0—7.8 (*ca.* 15H, m, Ph). ^{13}C NMR in $CDCl_3$, δ(ppm from internal Me_4Si): C^2 and C^4, 174.7q and 174.9q (J(C–F)=34 Hz); C^3, 89.9; C^6, 65.7; C^7, 64.8. Signals from C^1 and C^5 are not discernible because of overlapping with other signals.

(2,6-Diphenylpyridine-2C,N)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)palladium(II), *[Pd(hfac)(2,6-Ph$_2$-py-2C,N)]* (**9Dr**): The change with time of ^{1}H NMR spectrum in a $CDCl_3$ solution containing complex **1D** and equimolar 2,6-diphenylpyridine showed that the reaction to form **9Dr** and hfacH was completed after 16 h at 25 °C. Diethyl ether was added to the solution and the mixture was cooled to deposit yellow crystals of **9Dr** in *ca.* 80% yield. Found: C, 48.36; H, 2.38; N, 2.56%. Calcd for $C_{23}H_{13}NO_2F_6Pd$: C, 48.60; H, 2.41; N, 2.58%. Dec temp: 201—203 °C. IR in Nujol: ν(C=O)+ν(C=C), 1632vs, 1550s.

[2-(Dibenzylaminomethyl)phenyl](1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(triphenylphosphine)palladium(II), *[Pd(hfac)(2-Bz$_2$NCH$_2$C$_6$H$_4$)(PPh$_3$)]* (**10Dl**): Complex **9Dl** (129 mg, 0.215 mmol) readily reacted with triphenylphosphine (56 mg, 0.214 mmol) in dichloromethane at room temperature. After concentration of the solution by evaporation under reduced pressure, haxane was added to the concentrate and the mixture was cooled to precipitate yellow crystals (61 mg) in a 33% yield. Found: C, 61.23; H, 4.18; N, 1.50%. Calcd for $C_{44}H_{36}NO_2F_6PPd$: C, 61.30; H, 4.21; N, 1.62%. Dec temp: 145—148 °C. IR in Nujol: ν(C=O)+ν(C=C), 1675vs, 1525vs cm^{-1}. ^{1}H NMR in $CDCl_3$, δ (ppm from



internal Me_4Si): 3.91 (4H, s, $7CH_2$); 4.10 (2H, s, $6CH_2$); 5.21 (1H, s, 3CH); 6.4—7.6 (*ca.* 30H, m, Ph). ^{13}C NMR in $CDCl_3$, δ (ppm from internal Me_4Si): C^1 and C^5, 117.6 q (J(C–F)=290 Hz): C^2 and C^4, 173.9 q (J(C–F)=32 Hz); C^3, 86.0; C^6, 63.3; C^7, 59.6.

*Reaction of $[Pd(py)_4](tfac)_2 \cdot 3H_2O$ (**5Cm**) with Silver Nitrate.* A solution of silver nitrate (48 mg, 0.28 mmol) in pyridine (0.3 cm^3) was added to a solution of complex **5Cm** (82 mg, 0.10 mmol) in pyridine (0.5 cm^3) to deposit a white precipitate immediately, which was filtered, washed with benzene, and dried *in vacuo*. The yield of $[Pd(py)_4](NO_3)_2$ was 35 mg (62%). It is not soluble in organic solvents, but dissolves in hot water and gives white needles on cooling. The compound coincides with the authentic sample which was prepared by the reaction among sodium tetrachloropalladate(II), silver nitrate, and pyridine. Found: C, 43.92; H, 3.68; N, 15.60%. Calcd for $C_{20}H_{20}N_6O_6Pd$: C, 43.93; H, 3.69; N, 15.37%. IR in Nujol: $\nu(NO_3)$, 1376vs, br, 1325vs, br. ^1H NMR in D_2O at 75 °C, δ (ppm from internal DSS): 8.77 (2H, d, J=5 Hz, H^2 and H^6), 8.0 (1H), m, H^4), 7.6 (2H, m, H^3 and H^5).

Measurements. IR spectra were recorded in Nujol on Hitachi EPI-S2 and 295 spectrophotometers. NMR spectra were measured with JEOL JNM-C60HL and JNM-MH 100 (for ^1H), FX60Q (for ^1H and ^{13}C), and PS-100 (for ^{19}F) spectrometers. The molecular weight was determined by vapor pressure osmometry with an instrument manufactured by Knauer in West Berline, West Germany.

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