  Bull. Chem. Soc. Jpn., 57, 1850—1855 (1984)

Some Palladium(II) Complexes Containing Both the *O*-Unidentate β-Diketonato and 2-, 3-, or 4-Pyridyl Ligands. Dynamic Behaviors of *trans*-[Pd(β-dik-*O*)-(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$] in Solution

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(Received February 2, 1984)

Palladium(II) complexes of the [Pd(β-dik-*O*)(pyridyl)(PEt_3)$_2$] type containing an *O*-unidentate acetylacetonate, trifluoroacetylacetonate, or hexafluoroacetylacetonate anion and a 2-, 3-, 4-pyridyl or 6-chloro-2-pyridyl group as ligands were prepared and characterized mainly by ^{1}H and ^{13}C NMR spectroscopy. The acetylacetonate and hexafluoroacetylacetonate ligands in the [Pd(β-dik-*O*)(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$] complexes undergo the head-to-tail donor-atom exchange reaction, to which an intramolecular mechanism is proposed.

In a previous paper[1] a number of palladium(II) complexes containing an *O,O'*-chelating β-diketonate anion and a 2-, 3-, or 4-pyridyl group as ligands were prepared and characterized mainly by ^{1}H and ^{13}C NMR spectroscopy. Among these complexes [Pd(acac)-(C_5H_3(6-Cl)N-C^2)(PPh_3)] was found to undergo coordination site exchange catalyzed not only by usual free ligands such as tertiary phosphines, pyridine and its derivatives, but also by various donor solvents. Although the 6-chloro-2-pyridyl complex is stereochemically rigid by itself, the corresponding 2-pyridyl complex [Pd(acac)(C_5H_4N-C^2)(PPh_3)] partially dissociates in solution to liberate triphenylphosphine, which catalyzes the coordination-site exchange reaction of the parent complex, averaging the environments of two methyl groups of the acetylacetonate ligand (autocatalysis). Furthermore molecules of [Pd(acac)(C_5H_4N-C^3 or -C^4)(PPh_3)] were found to catalyze mutually their own coordination-site exchange (self-catalysis).

In the course of this investigation various pyridylpalladium(II) complexes containing an *O*-unidentate β-diketonate anion as a ligand were obtained. This paper reports on the preparation and characterization of these interesting compounds as well as dynamic behaviors of some of them in solution.

Experimental

Preparation of Complexes. The starting complexes [Pd(β-dik)(pyridyl)(PPh_3)] (β-dik=chelating anion of β-diketone (β-dikH) such as acetylacetone (acacH), trifluoroacetylacetone (tfacH), and hexafluoroacetylacetone (hfacH); pyridyl=C_5H_4N-C^2, C_5H_4N-C^3, C_5H_4N-C^4, or C_5H_3(6-Cl)-N-C^2) were prepared according to the methods reported previously.[1] Preparation of [PdBr(pyridyl)(PEt_3)$_2$] was also reported.[2] The present complexes [Pd(β-dik-*O*)(pyridyl)-(PEt_3)$_2$] containing an *O*-unidentate β-diketonate anion were prepared by two methods both in dichloromethane: (A) reactions of [Pd(β-dik)(pyridyl)(PPh_3)] with excess triethylphosphine, and (B) reactions of [PdBr(pyridyl)(PEt_3)$_2$] with Tl(β-dik). Here is described only a favorable method for each complex.

*[Pd(acac-O)(C_5H_4N-C^2)(PEt_3)$_2$] (**a1**): (Method A)*; Triethylphosphine (0.087 cm^3, 0.596 mmol) was added to a solution of [Pd(acac)(C_5H_4N-C^2)(PPh_3)] (0.109 g, 0.199 mmol) in dichloromethane (5 cm^3) and the mixture was stirred at room temperature for 30 min. After concentration to *ca.* 1 cm^3 by evaporation under reduced pressure, diethyl ether was added to the concentrate to deposit a white precipitate, which was filtered, washed with the ether and dried *in vacuo*. The product was purified by dissolution in dichloromethane followed by reprecipitation on addition of diethyl ether. The yield was 0.075 g (71.9%).

*[Pd(tfac-O)(C_5H_4N-C^2)(PEt_3)$_2$] (**a2**): (Method A)*; Complex **a2** was obtained in a 76.4% yield by the reaction between [Pd(tfac)(C_5H_4N-C^2)(PPh_3)] and PEt_3.

*[Pd(hfac-O)(C_5H_4N-C^2)(PEt_3)$_2$](**a3**): (Method B)*; A mixture of [PdBr(C_5H_4N-C^2)(PEt_3)$_2$] (0.309 g, 0.616 mmol) and Tl(hfac) (0.262 g, 0.636 mmol) in dichloromethane (10 cm^3) was stirred at room temperature for 50 min. After separation of thallium(I) bromide by filtration, the filtrate was concentrated to *ca.* 1 cm^3. On addition of petroleum ether (bp<60 °C) to the concentrate a precipitate appeared, which was filtered, washed with petroleum ether, and dried *in vacuo*. The yield was 0.272 g (68.1%).

*[Pd(acac-O)(C_5H_4N-C^3)(PEt_3)$_2$] (**b1**), [Pd(tfac-O)(C_5H_4N-C^3)(PEt_3)$_2$] (**b2**), and [Pd(hfac-O)(C_5H_4N-C^3)(PEt_3)$_2$] (**b3**)*: These complexes were similarly prepared by methods A, A, and B in 88.5, 88.0, and 37.7% yields, respectively. Complex **b3** is insoluble in usual organic solvents and precludes purification.

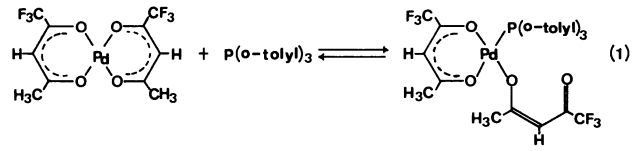
*[Pd(acac-O)(C_5H_4N-C^4)(PEt_3)$_2$] (**c1**), [Pd(tfac-O)(C_5H_4N-C^4)(PEt_3)$_2$] (**c2**), and [Pd(hfac-O)(C_5H_4N-C^4)(PEt_3)$_2$] (**c3**)*: Methods A, A, and B gave these complexes in 84.9, 91.9, and 42.6% yields, respectively.

*[Pd(acac-O)(C_5H_3(6-Cl)N-C^2)(PEt_3)$_2$] (**d1**), [Pd(tfac-O)(C_5H_3-(6-Cl)N-C^2)(PEt_3)$_2$](**d2**), and [Pd(hfac-O)(C_5H_3(6-Cl)N-C^2)-(PEt_3)$_2$] (**d3**)*: Complexes **d1** and **d2** were obtained by method A in 72.3 and 75.1% yields, respectively, while method B is preferable for compound **d3**. After filtration of thallium(I) chloride produced by the reaction between [PdCl(C_5H_3(6-Cl)N-C^2)PEt_3)$_2$] (0.269 g, 0.549 mmol) and Tl(hfac) (0.248 g, 0.603 mmol) in dichloromethane (10 cm^3) at room temperature, the solvent was vaporized *in vacuo* as far as possible. The residual mass was extracted with heptane. On standing the extract deposited a small additional amount of thallium(I) chloride, which was separated by filtration. The solvent was evaporated to dryness and the residue was dried at 50 °C *in vacuo*. The yield of **d3** was 0.261 g (71.8%).

Measurements. Infrared spectra were obtained in Nujol mull on a JASCO DS 701G spectrophotometer. The NMR spectra were recorded with JEOL JNM-MH100 (for ^{1}H) and FX 60Q (for ^{13}C and ^{31}P) spectrometers. Molecular weight was determined by vapor pressure osmometry with an instrument manufactured by Knauer in West Berlin, West Germany.

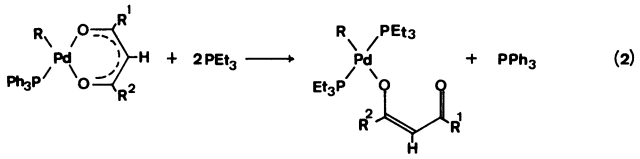
Results and Discussion

In recent years two of the present authors (S. K. and S. O.) and their coworkers studied extensively the reactions of [M(β-dik)$_2$] (M=Pd and Pt) with a variety of nitrogen bases,[3] tertiary phosphines,[4] and arsines.[4c] Among many kinds of products, some palladium(II) and platinum(II) complexes, [M(β-dik)(β-dik-*O*)L][4a] and [Pt(β-dik-*O*)$_2$L$_2$],[3c,4a] containing the *O*-unidentate β-diketonate ligand were obtained. Kinetics and equilibrium of the reaction between [Pd(tfac)$_2$] and P(*o*-tolyl)$_3$ to form [Pd(tfac)(tfac-*O*){P(*o*-tolyl)$_3$}] (Eq. 1)[5] and the crystal and molecular structure of the product[6] were also reported.



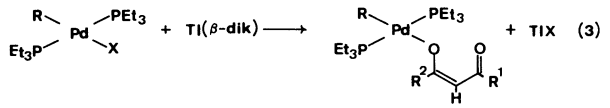
(1)

Now triethylphosphine reacted with [Pd(β-dik)(pyridyl)(PPh$_3$)] to convert the *O,O'*-chelated β-dik ligand into the *O*-unidentate state besides displacement of triphenylphosphine (Eq. 2, where R=pyridyl).

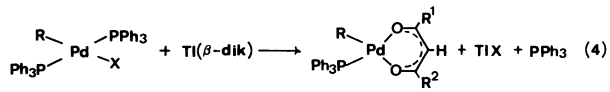


(2)

Although triethylphosphine was used in excess, other products such as [Pd(pyridyl)(PEt$_3$)$_3$](β-dik) and [Pd(pyridyl)(β-dik-*C*^{3})(PEt$_3$)$_2$] were not produced, but only the *O*-unidentate β-diketonato complexes were obtained in good yields. These complexes were also prepared by the reactions of [PdX(pyridyl)(PEt$_3$)$_2$] with Tl(β-dik) (Eq. 3), whereas the corresponding triphenylphosphine complexes [PdX(pyridyl)(PPh$_3$)$_2$] reacted with Tl(β-dik) to afford the β-dik chelates (Eq. 4).

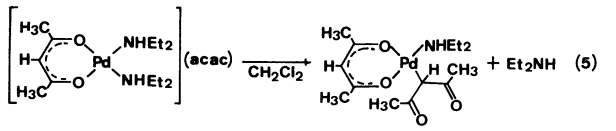


(3)

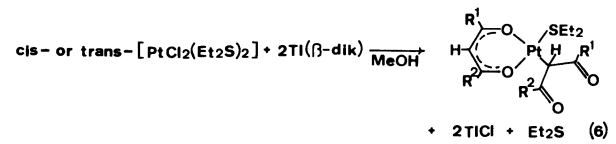


(4)

The Pd–PEt$_3$ bond seems to be stronger than Pd–PPh$_3$ and not cleaved by the intramolecular attack of the dangling carbonyl end of the *O*-unidentate β-diketonate ligand. It is worth noting that the β-diketonate anion is accepted as an *O*-unidentate ligand in the substitution reaction 3 irrespective of the nature of β-diketone (β-dik=acac, tfac, and hfac), whereas the central carbon bonding is prefered in many other reactions such as those exemplified by Eqs. 5[7] and 6 (β-dik=acac, tfac, or hfac).[8]



(5)



(6)

In the case of reaction 3 the carbon-bonded pyridyl ligand may exert trans influence to favor the *O*-bonding over the *C*-bonding of the β-diketonate anion. The PEt$_3$ ligands positioned mutually trans (*vide infra*) may also exert a steric influence on the entering β-diketonate ligand to favor the less bulky *O*-bonding. Results of elemental analysis and molecular weight determination of the newly prepared complexes are listed in Table 1.

^{1}H and ^{13}C NMR Spectra. The ^{1}H and ^{13}C{^{1}H} NMR data are collected in Tables 2 and 3, respectively. The latter data were obtained only for the 6-

Table 1. Analytical data for complexes [Pd(β-dik-*O*)(pyridyl)(PEt$_3$)$_2$]

No	β-dik	pyridyl	Found (Calcd)			
			C(%)	H(%)	N(%)	Mol wt[a]
a1	acac	C_5H_4N-*C*^{2}	50.44(50.82)	7.90(7.95)	2.71(2.69)	528(519.9)
a2	tfac	C_5H_4N-*C*^{2}	46.07(46.04)	6.62(6.67)	2.42(2.44)	582(573.9)
a3	hfac	C_5H_4N-*C*^{2}	41.50(42.09)	5.54(5.62)	2.24(2.23)	631(627.9)
b1	acac	C_5H_4N-*C*^{3}	50.69(50.82)	7.94(7.95)	2.63(2.69)	533(519.9)
b2	tfac	C_5H_4N-*C*^{3}	45.68(46.04)	6.63(6.67)	2.37(2.44)	589(573.9)
b3	hfac	C_5H_4N-*C*^{3}	41.24(42.09)	5.39(5.62)	2.28(2.23)	b)
c1	acac	C_5H_4N-*C*^{4}	50.87(50.82)	7.91(7.95)	2.72(2.69)	530(519.9)
c2	tfac	C_5H_4N-*C*^{4}	45.74(46.04)	6.54(6.67)	2.41(2.44)	575(573.9)
c3	hfac	C_5H_4N-*C*^{4}	41.37(42.09)	5.49(5.62)	2.23(2.23)	b)
d1	acac	C_5H_3(6-Cl)N-*C*^{2}	47.67(47.67)	7.28(7.27)	2.52(2.53)	550(554.4)
d2	tfac	C_5H_3(6-Cl)N-*C*^{2}	43.46(43.44)	6.12(6.13)	2.29(2.30)	613(608.3)
d3	hfac	C_5H_3(6-Cl)N-*C*^{2}	38.85(39.90)	5.15(5.17)	2.10(2.11)	663(662.3)

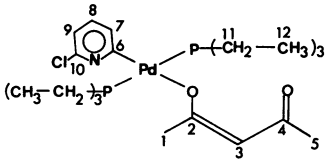
a) Determined in dichloromethane at 27 °C. b) Insoluble in organic solvents.

Table 2. ^{1}H NMR data in $CDCl_3$ at room temperature[a)]

Complex	β-dik		Pyridyl	PEt_3	
	CH_3	CH		CH_3	CH_2
a1	2.02, 2.36	5.87	6.68—7.26, 8.48 d	1.09 q	1.36 m
a2	2.43	5.95	6.65—7.36, 8.44 d	1.08 q	1.33 m
a3		5.54	6.65—7.35, 8.45 d	1.08 q	1.35 m
b1	2.01, 2.35	5.82	6.95 dd, 7.57 dd, 8.10 d, 8.50 s	1.10 q	1.37 m
b2	2.45	5.91	7.00 dd, 7.59 dd, 8.15 d, 8.51 s	1.10 q	1.35 m
c1	2.01, 2.34	5.79	7.30 d, 8.06 d	1.11 q	1.40 m
c2	2.45	5.91	7.33 d, 8.09 d	1.10 q	1.40 m
d1	2.03, 2.36	5.84	6.74—7.24	1.12 q	1.40 m
d2	2.42	5.92	6.72—7.20	1.09 q	1.34 m
d3		5.64	6.76 d, 7.04 t, 7.56 d	1.08 br	1.36 br

a) Chemical shifts in ppm from internal Me_4Si. s=singlet, d=doublet, t=triplet, q=1:4:6:4:1 quintet, m=multiplet, br=broad.

Table 3. $^{13}C\{^1H\}$ NMR data for $[Pd(\beta\text{-dik})(C_5H_3(6\text{-Cl})N\text{-}C^2)(PEt_3)_2]$[a)]



Complex	C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	C (7)	C (8)	C (9)	C(10)	C(11)	C(12)
d1[b)]	25.2	187.5	103.3	192.7	30.5	177.0 (5)	130.7 (6)	134.7	117.2	149.4	13.4 (12)	7.7
d2[b)]	27.3	195.9	96.1	174.2 [23]	119.1 [293]	175.0 (4)	130.6 (7)	135.0	117.6	149.6	13.4 (13)	7.6
d3[b)]	118.5 [289]	174.1 [32]	86.0	174.1 [32]	118.5 [289]	d)	130.4 (4)	134.5	117.4	149.1	13.8 (br)	7.3
d3[c)]	118.2 [290]	174.0 [30]	85.7	174.0 [30]	118.2 [290]	173.9 (4)	131.1 (7)	135.5	117.7	149.4	13.3 (12)	7.5

a) Chemical shifts in ppm from internal Me_4Si. Figures in parentheses and brackets give N(C-P) and J(C-F) in Hz, br=broad. b) Measured in $CDCl_3$ at room temperature. c) Measured in CD_2Cl_2 at −30 °C. d) Indiscernible because of a weak intensity and overlapping with signals from C(2).

chloro-2-pyridyl complexes which are sufficiently soluble in chloroform to allow the ^{13}C NMR measurements. The methyl-proton signal from the PEt_3 ligands in each complex appears as a 1:4:6:4:1 quintet and the methylene protons resonate as a multiplet. This spectral pattern is characteristic of the PEt_3 ligands situated mutually trans.[9)] The methylene carbons of the PEt_3 ligands in each of complexes **d1**, **d2**, and **d3** exhibit a triplet signal owing to coupling to the phosphorus atoms which are situated trans to each other and virtually coupling. In fact the $^{31}P\{^1H\}$ NMR spectra of **d1** and **d2** in $CDCl_3$ and of **d3** in CD_2Cl_2 show a singlet at 11.9, 12.0, and 9.5 ppm, respectively, downfield from external 85% H_3PO_4. The signal from **d3** is broad at room temperature (half-height width *ca.* 7 Hz) and becomes broader at higher temperature (half-height width at 60 °C *ca.* 14 Hz), while it sharpens at lower temperatures (half-height width at −30 °C *ca.* 2 Hz).

Figures 1, 2, and 3 compare the ^1H and $^{13}C\{^1H\}$ signals from the β-diketonate ligands in **d1**, **d2**, and **d3**. Of the two methyl-proton signals from complex **d1**, the lower-field one (δ2.36) is assigned to the methyl adjacent to the coordinated carbonyl group by reference to the data for $[Pt(acac\text{-}O)_2(piperidine)_2]$ which exhibits two methyl signals, one at 2.25 ppm[3c)] and the other flanked by ^{195}Pt satellites at 2.34 ppm.[3c)] The ^{13}C NMR data for the acac ligand in this platinum(II) complex (C^1 23.9, C^2 188.7, C^3 103.3, C^4 196.8, and C^5 30.6 ppm) are quite helpful for assignment of ^{13}C signals from **d1** (Table 3). The ^1H and ^{13}C NMR spectra of the *O*-unidentate tfac in **d2** (Fig. 2) also bear a close resemblance to those of the tfac-*O* ligands in $[Pt(\beta\text{-dik})(tfac\text{-}O)L]$ (β-dik=acac or tfac, L=PPh_3, P(*o*-tolyl)$_3$, or PEt_3), $[Pd(tfac)(tfac\text{-}O)L]$ (L=P(*o*-tolyl)$_3$ or P(cyclohexyl)$_3$), and $[Pt(tfac\text{-}O)_2(PEt_3)_2]$.[4a)]

Head-to-Tail Intramolecular Donor Atom Exchange of the O-Unidentate β-dik Ligands. Although the NMR spectra of **d1** and **d2** are satisfactorily interpreted on the basis that these complexes are stereochemically rigid in solution, complex **d3** shows only one set of signals from CF_3 and CO carbons (Fig. 3), indicating that **d3** is fluxional and the environments of both halves

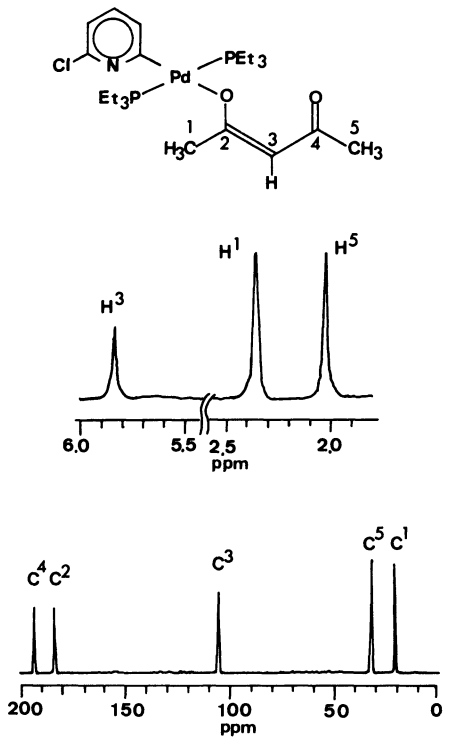
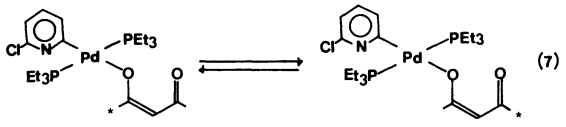


Fig. 1. ^{1}H and $^{13}C\{^{1}H\}$ NMR signals from the acetylacetonate ligand in [Pd(acac-*O*)(C_5H_3(6-Cl)N-C^2)-(PEt_3)$_2$] (**d1**) in $CDCl_3$ at room temperature. Chemical shifts are shown in ppm from internal Me_4Si.

of the *O*-unidentate hfac ligand are averaged rapidly on the NMR time scale. Unfortunately solubility of **d3** in dichloromethane is so poor at lower temperatures as to preclude the spectral determination below −30 °C, but the ^{13}C signals from the hfac-*O* ligand become broader with decreasing temperature and the carbonyl carbon signals show some indication of splitting.

As is seen in Fig. 4, the methyl-proton signals from the acac ligand in **d1** become sharper at 0 °C and broader at 50 °C, suggesting fluxional motion similar to that exhibited by **d3**. Complex **d1** as well as **d3** seems to undergo the head-to-tail intramolecular donor-atom exchange (Eq. 7), since no other change in spectrum is observed in this temperature range.



(7)

In order to study the fluxional motion of **d1** at higher temperatures *o*-dichlorobenzene was employed as solvent. A minor methyl signal appeared at 1.92 ppm besides the 2.11 and 2.56 ppm ones in this solvent at room temperature (Fig. 4). The chemical shift of this additional signal corresponds to average of methyl signals (1.90 and 1.94 ppm) of complex **d4**[1] in Eq. 8. In a previous paper triphenylphosphine was found to be a very effective catalyst for the coordination-site exchange reaction of [Pd(acac)(C_5H_3(6-Cl)N-C^2)(PPh_3)].[1] Triethylphosphine liberated by the chelate ring closure reaction (Eq. 8) seems to catalyze the coordination-site exchange of **d4**.

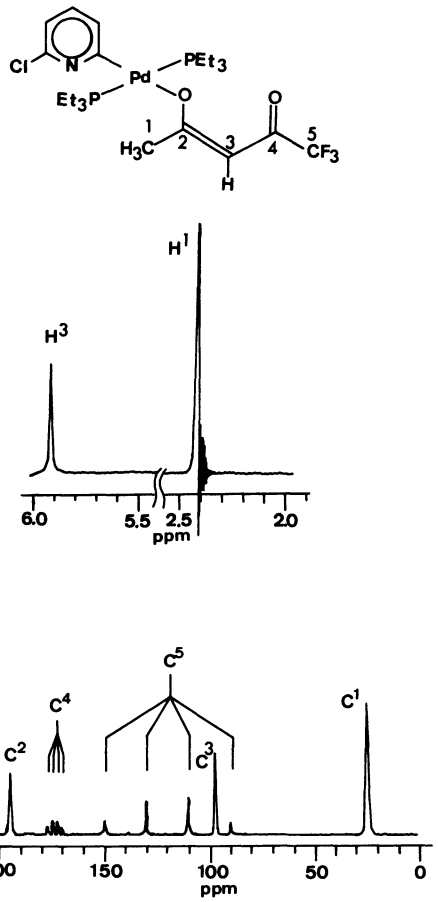
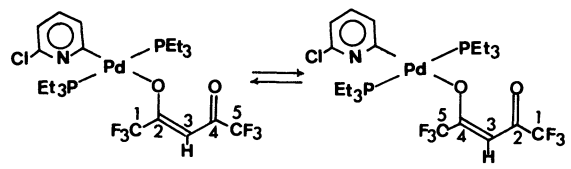


Fig. 2. ^{1}H and $^{13}C\{^{1}H\}$ NMR signals from the trifluoroacetylacetonate ligand in [Pd(tfac-*O*)(C_5H_3-(6-Cl)N-C^2)(PEt_3)$_2$] (**d2**) in $CDCl_3$ at room temperature. Chemical shifts are shown in ppm from internal Me_4Si.



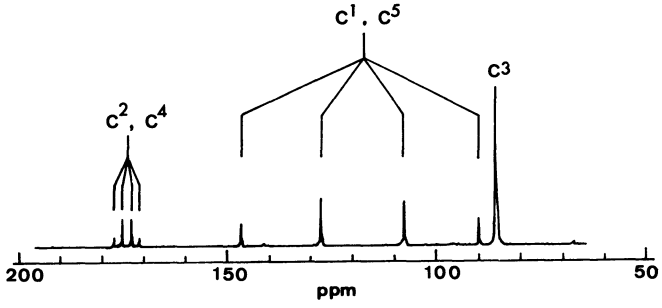


Fig. 3. $^{13}C\{^{1}H\}$ NMR signals from the hexafluoroacetylacetonate ligand in [Pd(hfac-*O*)(C_5H_3(6-Cl)N-C^2)-(PEt_3)$_2$] (**d3**) in $CDCl_3$ at room temperature. Chemical shifts are shown in ppm from internal Me_4Si.

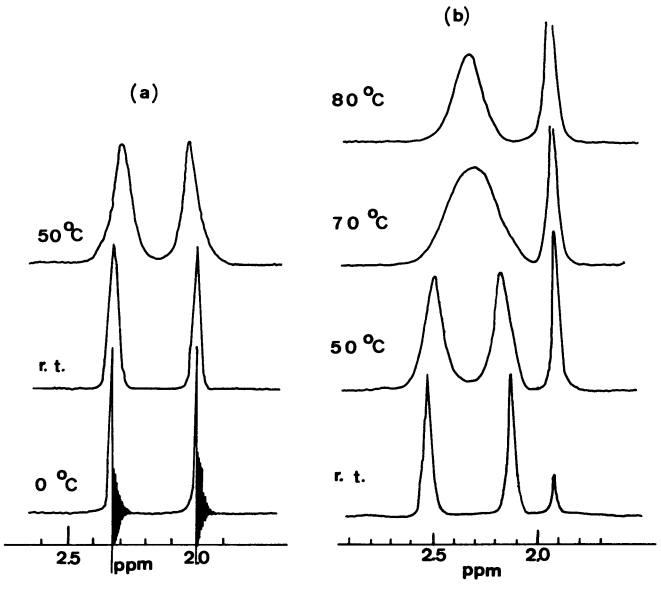
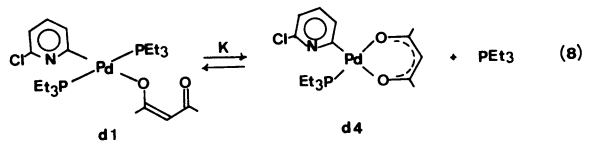
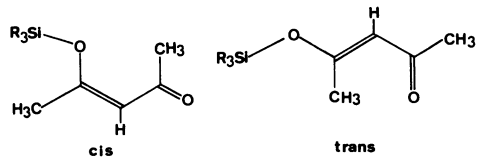


Fig. 4. ^{1}H NMR signals from the acetylacetonate ligand in [Pd(acac-*O*)(C_5H_3(C_5H_3(6-Cl)N-*C*^{2})(PEt_3)$_2$] (**d1**) in $CDCl_3$ (a) and *o*-dichlorobenzene (b) at several temperatures.



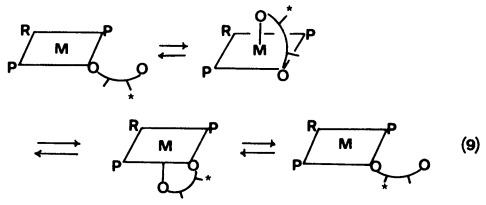
The equilibrium quotient K of reaction 8 was determined from the signal-area ratio to be 7.0×10^{-3} mol dm^{-3} at 33 °C. As is seen in Fig. 4, the δ1.92 signal becomes larger remarkably with temperature, K being 1.7×10^{-2}, 4.5×10^{-2}, 1.0×10^{-1}, and 2.2×10^{-1} mol dm^{-3} at 60, 70, 90, and 120 °C, respectively, and ΔH was obtained as 40.2 kJ mol^{-1}. Reaction 8 does not occur appreciably in chloroform and dichloromethane.

The ^{1}H NMR spectrum of R_3Si(acac-*O*) was found by Pinnavaia and his collaborators to be composed of signals from both cis and trans isomers.[10]



The trans isomer exhibits two methyl doublets and a methine multiplet owing to the spin-spin coupling between the methine and methyl protons, while the cis isomer shows a methyl singlet and a methine singlet without coupling. Equivalence of the two methyl groups in the cis isomer was thought to be caused by the intramolecular rearrangement *via* a trigonal-bipyramidal transition state involving the *O,O'*-chelated acetylacetonate anion.[10]

Complex **d1** shows only one methine singlet and two methyl signals with no sign of coupling indicating that the dangling acetyl group of the acac ligand is positioned cis to the coordinating oxygen atom with respect to the C=C bond. The same structure was also assigned to *trans*-[Pt(acac-*O*)$_2$(PEt_3)$_2$].[11] As is seen in Fig. 4 methyl signals become broader with increasing temperature and collapse at 70 °C. Above 80 °C one broad signal is observed. As a mechanism for the head-to-tail donor-atom exchange of the *O*-unidentate β-diketonate ligand in the present case, a simple oscillatory motion of the β-diketonate ligand spanning the apical and basal coordination sites in the square-pyramidal intermediate (Eq. 9) is proposed.



This kind of motion of a potentially bidentate ligand was previously assumed to explain the environmental equivalence of both halves of the essentially unidentate 1,10-phenanthroline in *cis*-[PtCl(phen)(PEt_3)$_2$]BF_4.[12] The X-ray molecular structures and solution behaviors of square-pyramidal complexes [Pt(hfac)$_2$(PCy_3)] and [Pd(hfac)$_2$\{P(*o*-tolyl)$_3$\}] were reported and the oscillatory motion depicted above was proposed as one of the two fluxional modes to average the environments of four CF_3 groups involved in the palladium(II) complex.[13]

Although the hfac anion gives these stable square-pyramidal platinum(II) and palladium(II) complexes in which one hfac anion spans the apical and basal coordination sites, the analogous reaction between [Pd(tfac)$_2$] and P(*o*-tolyl)$_3$ proceeds reversibly to afford [Pd(tfac)(tfac-*O*)\{P(*o*-tolyl)$_3$\}] (Eq. 1), exhibiting no spectral evidence for the five-coordinate intermediate.[5] No examples of square-pyramidal platinum(II) and palladium(II) complexes containing the acac ligand have been obtained either. These results suggest that the five-coordinate square-pyramidal intermediate as postulated in Eq. 9 will be most favorable for the hfac complex. It may be the reason why complex **d3** undergoes the fluxional motion much more readily than **d1** does.

We wish to thank Mr. Junichi Gohda for elemental analyses.

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