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Dinuclear Palladium(II) Complexes Containing Anilide Anions as Bridging Ligands

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The reactions of [Pd(hfac)$_2$] with aniline and its derivatives (L) in benzene at room temperature afforded [Pd(hfac)(hfac-C^3)L], [Pd(hfac)L$_2$](hfac), and [PdL$_4$](hfac)$_2$ depending on the reactants mole ratio. On the other hand, the reactions of various [Pd(β-dik)$_2$] complexes with L in refluxing benzene (in most cases) gave rise to the anilide-bridged dinuclear complexes [Pd(β-dik)(L−H)]$_2$, which in turn reacted with primary amines and pyridine (L′) to produce [PdL′$_2$(L−H)]$_2$(β-dik)$_2$.

Comprehensive investigations on the reactions of bis(β-diketonato)palladium(II) and -platinum(II), [M(β-dik)$_2$] (**1**), with various nitrogen bases[1] and tertiary phosphines[2] have revealed that the chelating β-diketonate anions are readily converted into other bonding states, affording a series of complexes, [M(β-dik)$_2$L] (**2**), [M(β-dik)(β-dik-*O*)L] (**3**), [M(β-dik)L$_2$](β-dik) (**4**), [ML$_4$](β-dik)$_2$ (**5**), [M(β-dik-*O*)$_2$L$_2$] (**6**), [M(β-dik)(β-dik-C^3)L] (**7**), and [M(β-dik-C^3)$_2$L$_2$] (**8**) depending on the natures of the metal, β-dik, and Lewis base (L). Here, β-dik, β-dik-*O*, and β-dik-C^3 in the coordination sphere represent the chelating, O-unidentate, and central-carbon-bonded states, respectively, β-dik in the outer sphere acting as a counter anion.

Characteristics of β-diketones (β-dikH) in keto-enol tautomerization and acid dissociation as well as the basicities and steric requirements of Lewis bases are the most important factors influencing the preference of bonding modes. Less basic β-dik ligands are readily displaced by L to outer sphere, while the keto-favorable β-dik anions prefer the carbon bonding. Thus, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), which exists solely as enol and is strongly acidic, has not given the carbon-bonded complexes **7** and **8**.[1,2]

This paper reports the reactions of [Pd(β-dik)$_2$] with aniline and its derivatives which afford complexes **7** as well as **4** and **5** at room temperature and the anilide-bridged dinuclear complexes at higher temperatures. Dialkylamide and disilylamide complexes of early transition metals are well-known[3] but those of the d^8 metals are rather scanty, and the amide-bridged dinuclear palladium(II) complexes reported in this paper are the first examples.

Experimental

Preparation of Complexes. The starting bis(β-diketonato)palladium(II) complexes were prepared by the methods reported recently.[4] Aniline and its derivatives were used as supplied without further purification but some samples which had been stored for a good while were purified by the method analogous to that employed for purification of aniline.[5]

Bis(aniline)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)palladium(II) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate–Benzene (2/1), [Pd(hfac)(C$_6$H$_5$NH$_2$)$_2$](hfac)·1/2C$_6$H$_6$ (4a): On addition of a benzene solution (1 cm^3) of aniline (233 mg, 2.50 mmol) to a solution of [Pd(hfac)$_2$] (**1a**) (325 mg, 0.624 mmol) in benzene (5 cm^3), color of the solution changed immediately from orange yellow to red and orange crystallites began to deposit. After being left overnight, the crystals were filtered, washed with petroleum ether (bp<50 °C) and dried *in vacuo*. The product (306 mg) was recrystallized from hot benzene. The final yield of red-orange plates was 237 mg (51%). Hexane was added to the filtrate and the mixture was left to stand for a week. Yellow plates deposited were filtered, washed with a mixture (1: 1 by volume) of benzene and hexane, dried *in vacuo* and characterized to be [Pd(C$_6$H$_5$NH$_2$)$_4$](hfac)$_2$ (**5a**), of which the yield was 124 mg (22%).

[Pd(hfac)(2,5-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_2$](hfac) (4b): Hexane (1 cm^3) was added to a mixture of **1a** (89 mg, 0.17 mmol) and 2,5-dimethylaniline (41 mg, 0.34 mmol) in benzene (2.5 cm^3) and the solvent mixture was allowed to vaporize spontaneously to leave an orange-red crystalline solid, which was washed with petroleum ether and dried *in vacuo*. The yield was 14 mg (11%).

[Pd(hfac)(2,6-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_2$](hfac)·H$_2$O (4c) and [Pd(hfac)(3,5-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_2$](hfac) (4d): Orange crystallites of **4c** and orange-red plates of **4d** were obtained in 88 and 92% yields, respectively, by the reactions of **1a** with twice molar amounts of 2,6- and 3,5-dimethylanilines in benzene at room temperature.

[Pd(hfac)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NH$_2$)$_2$](hfac)·H$_2$O (4e): A benzene solution (6 cm^3) containing **1a** (322 mg. 0.619 mmol) and 2,4,6-trimethylaniline (168 mg, 1.24 mmol) was heated under reflux for 2.5 h and then concentrated to 1 cm^3 by evaporation under reduced pressure. After being left overnight at room temperature, big orange crystals were filtered, washed with petroleum ether, and dried *in vacuo*. The yield was 339 mg (68%).

[Pd(hfac)(3-CF$_3$C$_6$H$_4$NH$_2$)$_2$](hfac) (4f): Hexane (0.2 cm^3) was added to a benzene solution (1 cm^3) containing **1a** (40 mg, 0.077 mmol) and 3-(trifluoromethyl)aniline (91 mg, 0.56 mmol) and the mixture was kept in a refrigerator to deposit orange plates (42 mg) in a 65% yield.

Tetrakis(aniline)palladium(II) 1,1,1,5,5,5-Hexafluoro-2,4-pentanedionate, [Pd(C$_6$H$_5$NH$_2$)$_4$](hfac)$_2$ (5a): Pale yellow plates of **5a** were obtained by addition of hexane (1 cm^3) to a mixture of **1a** (55 mg, 0.11 mmol) and aniline (77 mg, 0.83 mmol) in benzene (1.5 cm^3). The crystals lost lattice solvent to turn opaque on being dried *in vacuo*. The yield was 68 mg (72%).

[Pd(2-CH$_3$C$_6$H$_4$NH$_2$)$_4$](hfac)$_2$ (5b): When a solution (0.5 cm^3) of 2-methylaniline (27 mg, 0.25 mmol) in diethyl ether was added to a solution (0.5 cm^3) of **1a** (35 mg, 0.067 mmol) in the same solvent, color of the solution changed from orange to orange red, depositing yellow crystals, which were filtered, washed with diethyl ether and air-dried. The yield was 55 mg (86%). Recrystallization was performed from dichloromethane–petroleum ether.

[Pd(4-CH$_3$C$_6$H$_4$NH$_2$)$_4$](hfac)$_2$ (5c): 4-Methylaniline (98 mg, 0.91 mmol) was added to a suspension of **1a** (97 mg,

0.19 mmol) in benenze (1 cm^3) to result in a clear orange solution and deposit soon a pale yellow precipitate, which was filtered, washed with benzene and dried *in vacuo*. The yield was 90 mg (51%). Recrystallization from dichloromethane gave yellow plates.

*[Pd(2,4-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_4$](hfac)$_2$ (**5d**), [Pd(2,5-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_4$](hfac)$_2$ (**5e**), and [Pd(3,5-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_4$](hfac)$_2$ (**5f**)*: A benzene solution (2 cm^3) of **1a** (74 mg, 0.14 mmol) and 2,4-dimethylaniline (66 mg, 0.54 mmol) was allowed to stand overnight to produce yellow crystals of **5d**. The yield was 91 mg (64%). When 2,5- or 3,5-dimethylaniline was used as a base, a benzene solution containing **1a** and each of these anilines in the mole ratio of 1 : 4 was left at room temperature until the solvent vaporized spontaneously to leave a yellow crystalline solid of **5e** or yellow plates of **5f** in an 85 or 57% yield, respectively.

*2,6-Dimethylaniline(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-C^3)palladium(II), [Pd(hfac)(hfac-C^3)(2,6-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)] (**7a**)*: A benzene solution (1 cm^3) of 2,6-dimethylaniline (70 mg, 0.58 mmol) was added to a benzene solution (10 cm^3) of **1a** (298 mg, 0.573 mmol) and the solvent was allowed to evaporate spontaneously to leave orange-red columns, which were washed with benzene and dried *in vacuo*. The yield was 358 mg (97%). This compound is sparingly soluble in organic solvents.

*[Pd(hfac)(hfac-C^3)(3,5-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)] (**7b**)*: When a benzene solution (1 cm^3) of 3,5-dimethylaniline (42 mg, 0.35 mmol) was added to a benzene solution (2 cm^3) of **1a** (178 mg, 0.342 mmol), color of the solution changed gradually from orange yellow to orange red and orange-red crystals began to deposit. After being left overnight the precipitate was filtered, washed with benzene and dried *in vacuo*. The yield was 92 mg (42%).

*[Pd(hfac)(hfac-C^3)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NH$_2$)] (**7c**)*: When a mixture of **1a** (509 mg, 0.978 mmol) and 2,4,6-trimethylaniline (135 mg, 0.998 mmol) in benzene (12 cm^3) was heated under reflux for 2.5 h, color of the solution changed gradually from orange yellow to dark red. The solution was then concentrated to 3 cm^3 by evaporation under reduced pressure. Hexane (2 cm^3) was added to the concentrate and the solvent mixture was allowed to vaporize spontaneously to leave orange-red columns, which were washed with diethyl ether (5 cm^3) and air-dried. The yield was 365 mg. The washings were allowed to vaporize spontaneously, leaving another crop of **7c**, which was filtered and washed with a mixture (1 : 1 by volume) of diethyl ether and petroleum ether. The total yield was 447 mg (70%).

*Di-μ-anilidobis(2,4-pentanedionato)dipalladium(II), [Pd(acac)(C$_6$H$_5$NH)]$_2$ (**9a**)*: Aniline (98 mg, 1.05 mmol) was added to a benzene solution (5 cm^3) of [Pd(acac)$_2$] (**1b**) (42 mg, 0.14 mmol) and the mixture was heated under reflux for 7 h. The solvent was then distilled away under reduced pressure to leave a red-brown powder, which was washed with diethyl ether and air-dried. The yield was 16 mg (39%). Very low solubility of **9a** prevented recrystallization.

*[Pd(acac)(2-CH$_3$C$_6$H$_4$NH)]$_2$ (**9b**)*: A benzene solution containing **1b** and excess 2-methylaniline was refluxed for 30 min and cooled to room temperature to deposit a red-brown precipitate, which was filtered, washed with petroleum ether, and then recrystallized from hot benzene. The yield was 92%.

*[Pd(acac)(2,5-(CH$_3$)$_2$C$_6$H$_3$NH)]$_2$ (**9c**)*: 2,5-Dimethylaniline (1.58 g, 13.0 mmol) was added to a benzene solution (5 cm^3) of **1b** (405 mg, 1.33 mmol) and the mixture was refluxed for 8 h. The solvent was then distilled away under reduced pressure, leaving an orange powder behind, which was washed with petroleum ether and dried *in vacuo*. The same compound was obtained by spontaneous evaporation of the washings. The total yield of **9c** was 295 mg (68%). With an aim of recrystallization, the product was dissolved in hot dichloromethane (10 cm^3) and the solution was kept in a refrigerator overnight to deposit red plates (**9c**-α; 62 mg, 13%), which were filtered, washed with diethyl ether, and air-dried. The filtrate was kept further in a refrigerator to precipitate orange needles (**9c**-β; 68 mg, 16%), which was filtered, washed with diethyl ether, and air-dried. Red plates were analysed to contain one half molecule of dichloromethane per palladium as the lattice solvent and orange needles to contain one sixth molecule of dichloromethane. Results of the elemental analysis indicate that these two compounds are isomers (*vide infra*). The α-form is more soluble than the β-form in chloroform and dichloromethane.

*[Pd(acac)(2,6-(CH$_3$)$_2$C$_6$H$_3$NH)]$_2$ (**9d**), [Pd(acac)(2-C$_2$H$_5$C$_6$H$_4$NH)]$_2$ (**9e**), [Pd(acac)(C$_{10}$H$_7$-1-NH)]$_2$ (**9f**), and [Pd(acac)(5-NH$_2$C$_{10}$H$_6$-1-NH)]$_2$ (**9g**)*: The reactions of **1b** with 2,6-dimethylaniline, 2-ethylaniline, 1-naphthylamine, and 1,5-naphthalenediamine were carried out in a similar way to the case of **9b** and the orange-red products were recrystallized from hot benzene, the yields being *ca.* 3, 56, 11, and 98%, respectively.

*Di-μ-anilidobis(1-phenyl-1,3-butanedionato)dipalladium(II), [Pd(bzac)(C$_6$H$_5$NH)]$_2$ (**9h**)*: On addition of excess aniline (*ca.* 0.2 cm^3) to a solution of [Pd(bzac)$_2$] (101 mg, 0.236 mmol) in dichloromethane (3 cm^3), color of the solution changed from orange yellow to red. A small amount of petroleum ether was added to the solution and the solvent mixture was allowed to evaporate spontaneously to leave an orange residue, which was washed with diethyl ether. The yield was 80 mg (94%).

*Di-μ-anilidobis(1,1,1-trifluoro-2,4-pentanedionato)dipalladium(II), [Pd(tfac)(C$_6$H$_5$NH)]$_2$ (**9i**)*: Excess aniline was mixed with [Pd(tfac)$_2$] (**1c**) (351 mg, 0.851 mmol) in dichloromethane (10 cm^3) and the solvent was vaporized spontaneously to leave a red crystalline solid on the wall and a red oily substance at the bottom of the vessel. The solid was washed with methanol. The oil was dissolved in dichloromethane. Hexane was added to the solution and the mixture was cooled to deposit a red crystalline solid, which was filtered and washed with methanol. The two specimens gave the same IR spectra. After drying *in vacuo*, the total yield was 175 mg (58%). Recrystallization from *N,N*-dimethylformamide gave brown needles of **9i**. On the other hand, the combined washings were kept in a refrigerator for 6 h to precipitate orange-yellow needles of Shiff base complex, *bis(4-phenylamino-1,1,1-trifluoro-3-penten-2-onato)palladium(II) [Pd{N(C$_6$H$_5$)C(CH$_3$)CHCOCF$_3$}$_2$] (**11**)*, which were filtered, washed with methanol, and dried *in vacuo*. The yield of **11** was 10%. Recrystallization was performed from methanol or dichloromethane. Found: C, 47.32; H, 3.35; N, 5.03%. Calcd for $C_{22}H_{18}N_2O_2F_6Pd$: C, 46.95; H, 3.22; N, 4.98%. IR in Nujol: ν(C=O)+ν(C=C)+ν(C=N), 1616 vs, 1586 m, 1524 vs; no ν(NH) band.

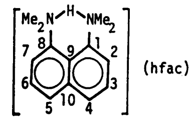
*[Pd(tfac)(2-CH$_3$C$_6$H$_4$NH)]$_2$ (**9j**), [Pd(tfac)(4-CH$_3$C$_6$H$_4$NH)]$_2$ (**9k**), and [Pd(tfac)(2,6-(CH$_3$)$_2$C$_6$H$_3$NH)]$_2$ (**9l**)*: The reactions of **1c** with three times molar 2-methylaniline, equimolar 4-methylaniline, and excess 2,6-dimethylaniline in refluxing benzene for several hours followed by spontaneous evaporation of the solvent gave **9j**, **9k**, and **9l** as an orange powder, orange-yellow needles, and orange-red needles in 32, 34, and several percent yields, respectively.

*[Pd(hfac)(2-CH$_3$C$_6$H$_4$NH)]$_2$ (**9n**)*: A mixture of **1a** (497 mg, 0.955 mmol) and 2-methylaniline (103 mg, 0.963 mmol) in benzene (10 cm^3) was heated under reflux for 7 h and then concentrated to 2 cm^3 by evaporation under reduced pressure. Hexane (several cm^3) was added to the concentrate and the

mixture was left to stand for three days to deposit dark red needles, which were filtered, washed with hexane and dried *in vacuo*. The yield was 295 mg (74%).

[Pd(hfac)(C$_6$H$_5$NH)]$_2$ (9m) and [Pd(hfac)(4-CH$_3$C$_6$H$_4$NH)]$_2$ (9o): These complexes were obtained in a similar manner as above as dark red crystals in 55 and 25% yields, respectively.

Alternatively, employment of 1,8-bis(dimethylamino)-naphthalene, "proton sponge," greatly enhanced the reaction of **1a** with 4-methylaniline to form **9o**. After addition of "proton sponge" (87 mg, 0.41 mmol) to a chloroform solution (1.5 cm^3) of **1a** (207 mg, 0.398 mmol) and 4-methylaniline (43 mg, 0.40 mmol), the solvent was distilled away under reduced pressure and the residue was washed with a mixture (1 : 1 by volume) of methanol and water, and dried *in vacuo*. The yield of a red-brown powder was 148 mg (88%). The washings were vaporized under reduced pressure and the residue was recrystallized from methanol–water. Pale yellow columns (46 mg) were identified to be the naphthylammonium salt of hfac (**12**) based on the following analytical and spectroscopic data and the yield was 27%. Found: C, 54.15; H, 4.80; N, 6.66%. Calcd for C$_{19}$H$_{20}$N$_2$O$_2$F$_6$: C, 54.03; H, 4.77; N, 6.63%. Dec temp (sublimation) 105—130 °C. IR in Nujol: ν(C=C)+ν(C=O) 1675 vs, 1550 vs, and 1530 s; ν(C–F) 1250 vs, 1172 vs, 1145 vs, 1123 vs. NMR in CDCl$_3$ (δ, ppm from internal Me$_4$Si), ^{1}H: 3.29d (12H, N–CH$_3$, J(NH–CH$_3$)$=1._2$ Hz), 5.68s (1H, hfac-CH), *ca.* 7.8 m (6H, ring-CH), 18.6 br (1H, N–H–N); ^{13}C: 118.4 q (CF$_3$, ^1J(C–F) =292 Hz), 173.5 q (CO, ^2J(C–F)=30 Hz), 84.2 (hfac-CH, ^1J(C–H)=159 Hz), 46.6 (CH$_3$, ^1J(C–H)=140 Hz), 144.8 (C^1, C^8), 120.9 (C^2, C^7, ^1J (C–H)=159 Hz), 129.2 (C^3, C^6, ^1J (C–H)=164 Hz), 126.9 (C^4, C^5, ^1J (C–H)=160 Hz), 118.9 (C^9), 135.5 (C^{10}). (Ring-carbon assignments are tentative.)



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[Pd(hfac)(2,5-(CH$_3$)$_2$C$_6$H$_3$NH)]$_2$ (9p) and [Pd(hfac)(2,6-(CH$_3$)$_2$C$_6$H$_3$NH)]$_2$ (9q): The reactions of **1a** with equimolar 2,5-dimethylaniline and 2,6-dimethylaniline were allowed to proceed in refluxing benzene for 1 and 2 h, respectively. After evaporation of the solvent, residues were treated with hexane and methanol, respectively. Dark red needles of **9p** and a dark red powder of **9q** were obtained in 68 and 60% yields, respectively. Compound **9q** was also obtained as orange-red needles in a 9% yield when **7a** was dissolved in methanol and the solution was left to stand at room temperature.

[Pd(hfac)(3,5-(CH$_3$)$_2$C$_6$H$_3$NH)]$_2$ (9r): The reaction of **1a** with equimolar 3,5-dimethylaniline in refluxing toluene for 1.5 h and work up similar to the case of **9n** gave dark red needles in a 57% yield.

[Pd(hfac)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NH)]$_2$ (9s): Compound **7c** (20 mg, 0.031 mmol) was dissolved in hot methanol (1 cm^3) and the solution was left to stand at ambient temperature to deposit orange-red plates, which were filtered, washed with hexane and dried *in vacuo*. The yield was 5 mg (36%).

[Pd(hfac)(3-CF$_3$C$_6$H$_4$NH)]$_2$ (9t): A benzene solution (5 cm^3) of **1a** (138 mg, 0.265 mmol) and 3-(trifluoromethyl)-aniline (43 mg, 0.27 mmol) was refluxed for 1.5 h and then concentrated to 1 cm^3 by evaporation under reduced pressure. Petroleum ether (several cm^3) was added to the concentrate and the mixture was left to stand for a week at room temperature to deposit a red-orange crystalline solid, which was filtered and washed with petroleum ether. The yield was 90 mg (72%). Recrystallization from dichloromethane–petroleum ether gave a mixture of red plates (α-form) and dark red column (β-form), which was filtered, washed with petroleum ether, and air-dried. Manual separation gave **9t-α** (20 mg) and **9t-β** (34 mg) in 16 and 27% yields, respectively.

[Pd(hfac)(2-NO$_2$C$_6$H$_4$NH)]$_2$ (9u): Hexane (several cm^3) was added to a benzene solution (2.5 cm^3) of **1a** (81 mg, 0.16 mmol) and 2-nitroaniline (22 mg, 0.16 mmol) and the mixture was left to stand for five days to precipitate red needles, which were filtered, washed with petroleum ether, and dried *in vacuo*. The washings were evaporated spontaneously to separate another crop. The total yield was 34 mg (48%).

[Pd(hfac)(4-NO$_2$C$_5$H$_4$NH)]$_2$ (9v): 4-Nitroaniline (39 mg 0.28 mmol) was allowed to react with **1a** (146 mg, 0.281 mmol) in refluxing dichloromethane (2 cm^3) for 3 h. The solvent was then distilled away under reduced pressure and the residue was recrystallized from dichloromethane–petroleum ether to give red plates. Another crop of red crystalline solid was also obtained by cooling the filtrate. The total yield was 85 mg (67%).

Di-μ-anilidotetrakis(propylamine)dipalladium(II) 1,1,1-Trifluoro-2,4-pentanedionate, [Pd(C$_6$H$_5$NH)(n-PrNH$_2$)$_2$]$_2$(tfac)$_2$ (10a): Complex **9i** (61 mg, 0.087 mmol) was dissolved in propylamine (0.5 cm^3) and the excess amine was allowed to evaporate spontaneously to leave a yellow crystalline solid (64 mg) in a 78% yield.

[Pd(C$_6$H$_5$NH)(py)$_2$]$_2$(tfac)$_2$·2H$_2$O (10b): Complex **9i** was dissolved in a minimum amount of pyridine and diethyl ether was added to the solution. On cooling the mixture, yellow columns appeared, which were filtered, washed with diethyl ether, and dried *in vacuo*. The yield was about 50%.

[Pd(4-CH$_3$C$_6$H$_4$NH)(4-CH$_3$C$_6$H$_4$NH$_2$)$_2$]$_2$(tfac)$_2$·1/2 C$_6$H$_6$ (10c): 4-Methylaniline (76 mg, 0.71 mmol) reacted with **1c** (81 mg, 0.20 mmol) in benzene (1.5 cm^3) at room temperature to deposit orange crystals, which were filtered, washed with hexane, and dried *in vacuo*. The yield was 73 mg (62%).

[Pd(2-CH$_3$C$_6$H$_4$NH)(2-CH$_3$C$_6$H$_4$NH$_2$)$_2$]$_2$(hfac)$_2$ (10d): A mixture of complex **9n** (123 mg, 0.146 mmol) and 2-methylaniline (93 mg, 0.87 mmol) in benzene (5 cm^3) was heated under reflux for 4.5 h and concentrated by evaporation under reduced pressure to deposit a yellow-brown crystalline solid, which was filtered, washed with petroleum ether, and dried *in vacuo*. The yield was 108 mg (58%).

[Pd(2-CH$_3$C$_6$H$_4$NH)(3,5-(CH$_3$)$_2$C$_6$H$_3$NH$_2$)$_2$]$_2$(hfac)$_2$ (10e): 3,5-Dimethylaniline (75 mg, 0.62 mmol) was added to a benzene solution (5 cm^3) of **9n** (65 mg, 0.077 mmol) and the mixture was left to stand at room temperature to deposit a yellow-brown precipitate. The solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane–petroleum ether to give orange tiny crystals (46 mg) in a 45% yield.

[Pd(2-CH$_3$C$_6$H$_4$NH)(CH$_3$NH$_2$)$_2$]$_2$(hfac)$_2$ (10f): Complex **9n** was dissolved in methylamine and the excess amine was removed under reduced pressure to leave a yellow powder of **10f** in a quantitative yield.

[Pd(2-CH$_3$C$_6$H$_4$NH)(n-PrNH$_2$)$_2$]$_2$(hfac)$_2$·2H$_2$O (10g): Complex **9n** (54 mg, 0.064 mmol) was dissolved in propylamine (3 cm^3) and the excess amine was vaporized spontaneously. The residue was washed with hexane and dried *in vacuo* to give a yellow powder (31 mg) in a 44% yield. Yellow columns were obtained by recrystallization from dichloromethane–petroleum ether.

[Pd(2-CH$_3$C$_6$H$_4$NH)(py)$_2$]$_2$(hfac)$_2$ (10h): Small amounts

of diethyl ether and hexane were added to a solution of **9n** (23 mg, 0.027 mmol) in pyridine (0.1 cm^3) and the mixture was cooled to deposit a yellow precipitate, which was filtered, washed with diethyl ether, and dried *in vacuo*. Although solubilities in usual solvents are low, recrystallization was possible from dichloromethane–petroleum ether. The yield was very low (less than 10%).

$[Pd(3,5\text{-}(CH_3)_2C_6H_3NH)(3,5(CH_3)_2C_6H_3NH_2)_2]_2(hfac)_2$ *(10i)*: 3,5-Dimethylaniline (34 mg, 0.28 mmol) was added to a benzene solution (2 cm^3) of complex **9r** (56 mg, 0.065 mmol) and the mixture was left to stand at room temperature for three days to deposit an orange precipitate, which was filtered, washed with hexane, and dried *in vacuo*. The yield was 42 mg (48%).

Measurements. IR spectra were recorded in Nujol mull on Hitachi EPI-S2 and 295 spectrophotometers. NMR spectra were measured with JEOL-C60 HL (^{1}H), FX60Q (^{1}H and ^{13}C), and PS-100 (^{19}F) spectrometers. The molecular weight was determined in dichloromethane at room temperature by vapor pressure osmometry with an instrument manufactured by Knauer in West Berline, West Germany.

Results and Discussion

Table 1 shows the analytical data for most of the newly prepared complexes together with their decomposition temperatures, but data for twelve compounds were omitted for brevity. The reactions of [Pd(hfac)$_2$] (**1a**) with aniline and its derivatives (L) mostly in benzene at room temperature afforded [Pd(hfac)L$_2$](hfac) (**4**) and [PdL$_4$](hfac)$_2$ (**5**) when twice molar and more than

Table 1. Analytical data for newly prepared complexes, [Pd(hfac)L$_2$](hfac) (**4**), [PdL$_4$](hfac)$_2$ (**5**), [Pd(hfac)(hfac-*C*^{3})L] (**7**), [Pd(*β*-dik)(L−H)]$_2$ (**9**), and [PdL'$_2$(L−H)]$_2$(*β*-dik)$_2$ (**10**)

Compd	Dec pt / °C	Found (Calcd) (%) C	H	N
4a[a]	*ca.* 96	40.29 (40.26)	2.56 (2.57)	3.93 (3.76)
4c[b]	164—165	40.13 (39.98)	3.42 (3.36)	3.75 (3.59)
4d[c]	122—123	41.06 (40.93)	3.25 (3.17)	3.70 (3.67)
4e[b]	98—100	41.61 (41.57)	3.73 (3.74)	3.31 (3.46)
5a[c]	106—110	45.77 (45.73)	3.36 (3.39)	6.51 (6.27)
5b	115—116[d]	48.51 (48.09)	4.22 (4.04)	5.98 (5.90)
5c	118—119	48.02 (48.09)	4.08 (4.04)	5.89 (5.90)
5f	134—135	50.26 (50.18)	4.68 (4.61)	5.55 (5.57)
7a	116—117[d]	33.85 (33.69)	2.10 (2.03)	2.05 (2.18)
7b	101—102	33.42 (33.69)	1.94 (2.04)	2.19 (2.18)
7c	97—100[d]	34.86 (34.80)	2.31 (2.31)	2.07 (2.14)
9a	214—218	43.95 (44.39)	4.34 (4.40)	4.64 (4.71)
9b	*ca.* 208	46.84 (46.25)	4.90 (4.85)	4.58 (4.50)
9c-*α*[e]	*ca.* 180	46.20 (45.87)	5.09 (5.08)	4.01 (4.04)
9c-*β*[f]	213—214	47.20 (47.22)	5.22 (5.20)	3.90 (4.21)
9d	*ca.* 198	48.31 (47.94)	5.31 (5.26)	4.46 (4.30)
9e	*ca.* 218	47.95 (47.94)	5.32 (5.26)	4.43 (4.30)
9f	*ca.* 190	52.53 (51.82)	4.36 (4.34)	4.02 (4.02)
9h	*ca.* 240	53.41 (53.42)	4.23 (4.20)	3.87 (3.89)
9i	*ca.* 216[d]	37.63 (37.57)	2.88 (2.87)	4.11 (3.98)
9m	*ca.* 183[d]	32.63 (32.58)	1.74 (1.74)	3.52 (3.45)
9n	*ca.* 187[d]	34.46 (34.35)	2.19 (2.16)	3.40 (3.34)
9o	*ca.* 85 (mp)	34.24 (34.35)	2.20 (2.16)	3.34 (3.34)
9p	*ca.* 165	36.03 (36.01)	2.54 (2.56)	3.13 (3.23)
9q	*ca.* 144[d]	35.89 (36.01)	2.56 (2.56)	3.24 (3.23)
9r	*ca.* 172[d]	35.85 (36.01)	2.50 (2.56)	3.40 (3.23)
9t-*α*	*ca.* 165[d]	30.37 (30.43)	1.19 (1.28)	2.89 (2.96)
9t-*β*	*ca.* 153[d]	30.53 (30.43)	1.27 (1.28)	2.91 (2.96)
9u	*ca.* 120	29.31 (29.32)	1.36 (1.34)	6.21 (6.22)
9v	*ca.* 210	29.36 (29.32)	1.36 (1.34)	6.18 (6.22)
10a	*ca.* 140	43.68 (43.46)	5.89 (6.01)	8.72 (8.94)
10b[g]	90— 95	47.99 (47.79)	4.26 (4.20)	8.01 (7.96)
10c[a]	190—195	54.91 (55.10)	5.59 (5.30)	6.86 (7.01)
10d	*ca.* 180	49.79 (49.26)	4.31 (4.29)	6.51 (6.63)
10g[g]	110—119	39.01 (38.89)	5.28 (5.26)	7.25 (7.56)
10i	*ca.* 150	51.27 (51.53)	4.94 (4.92)	5.97 (6.22)

a) Benzene solvate (one half molecule per Pd). b) Monohydrate. c) Crystals contain solvent of crystallization which is lost gradually at room temperature. Solvent-free specimens were analyzed which were obtained by pulverizing and through pumping. d) The compound sublimes at this temperature. e) Dichloromethane solvate (1/2 molecule per Pd). f) Dichloromethane solvate (1/6 molecule per Pd). g) Dihydrate.

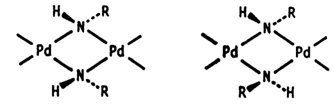
four times molar amounts of L was used, respectively, while the equimolar reaction gave rise to [Pd(hfac)-C^3)L] (**7**). The carbon-bonded complex of hfac has never been produced by the reactions of **1a** with alkylamines, pyridines, and tertiary phosphines.[1,2b)] Now the presence of type **7** complexes in the equimolar reaction mixtures of **1a** and various aniline derivatives was confirmed by the NMR assay, although isolation of the products was successful only for **7a**, **7b**, and **7c**. 2,6-Dimethyl- and 2,4,6-trimethylanilines gave type **4** and **7** complexes but do not produce **5** probably because of their large steric demands.

Refluxing of an equimolar mixture of **1a** and an aniline derivative L in benzene gave rise to dinuclear complexes [Pd(hfac)(L—H)]$_2$ (**9**) containing the bridging anilide anions (L—H). Complexes **9** were also derived spontaneously from **7** in methanol solutions. The reactions of other [Pd(β-dik)$_2$] complexes (β-dik= 2,4-pentanedionate (acac), 1-phenyl-1,3-butanedionate (bzac), and 1,1,1-trifluoro-2,4-pentanedionate (tfac) anions) with L did not give **4**, **5**, and **7**, but produced **9** exclusively. Solubilities of anilide complexes **9** in organic solvents are very low and somewhat improved by methy substitutions on thephenyl ring. The molecular weight of **9n** (842) determined in dichloromethane (0.005—0.05 mol dm^{-3}) coincides well with the value (839) calculated for the dinuclear structure, whereas those for **9c**-β (732) and **9i** (610) observed only for very dilute solutions are far less accurate and do not coincide with but are near the calculated values, 666 and 704, respectively. The analytical results in Table 1 together with these molecular-weight data accord with the dinuclear formulation of **9**, which is also supported by the NMR data reported below.

Deprotonation of amine groups coordinated to d^8 metals is usually effected by a strong base such as potassium amide in liquid ammonia,[6)] but the reaction of dichloro(2,2′-bipyridine)platinum(II) with *cis,cis*-1,3,5-triaminocyclohexane (tach) in aqueous solution was found to result in [Pt(bpy)(tach—2H)H$_2$O]Cl$_2$, an octahedral Pt(IV) complex containing the tach dianion as a terdentate ligand.[7)] In the present case, the coordinated aniline seems to be deprotonated by the β-diketonate anion situated in the inner or outer sphere (*vide infra*).

Although the hfac complexes **4** and **5** containing alkylamines as L are yellow and colorless, respectively,[1a)] the corresponding aniline complexes are generally reddish and complexes **9** are dark red. The dinuclear anilide complexes **9** are thermally stable and the hfac complexes except **9o** can be sublimed in accordance with the general trend that substitution of the methyl groups of acac with CF$_3$ increases volatility of the complex.[8)] The anilide-bridged dinuclear structure is very stable in solution, too. Treatment of complexes **9** with pyridine or primary amines (L′) does not effect cleavage of the bridge, but displaces the chelating β-dik ligands to produce [PdL′$_2$(L—H)]$_2$(β-dik)$_2$ (**10**). A platinum(II) complex containing an anilide anion as a unidentate ligand, *trans*-[PtCl(C$_6$H$_5$NH)(PEt$_3$)$_2$] was prepared by the reaction of *trans*-[PtH(Cl)(PEt$_3$)$_2$] with phenyl azide,[9)] and was treated with silver hexafluorophosphate in acetone.[10)] Abstraction of the chloride ligand did not occur, but oxidative coupling of the anilide was effected to result in a benzidine complex. The ancillary ligands may strongly affect the behavior of the anilide ligand.

Recrystallization of **9c** from dichloromethane gave two kinds of crystals, red plates and orange needles, containing different numbers of solvent molecules per palladium, which are tentatively designated as α and β forms, respectively. The two specimens **9c**-α and **9c**-β exhibit different IR and NMR spectra (*vide infra*) and seem to constitute a pair of isomers. The following two stereoisomers are conceivable for the di-μ-anilide structure, although it is difficult at present to identify which of **9c**-α and **9c**-β has the syn structure. Recrystallization of **9t** from dichloromethane–petroleum ether also gave both red plates and dark red columns. The IR spectra suggest that the former has the same structure as that of **9c**-α and the latter corresponds to the β form.



syn *anti*

When complex **9i** was prepared by the reaction of **1c** with aniline, complex **11** was obtained as a by-product and characterized by elemental analysis and IR spectroscopy. A Schiff base ligand 4-phenylamino-1,1,1-trifluoro-3-penten-2-one was prepared by Röhrscheid *et al.*[11)] according to a previous method for 4-phenylamino-3-penten-2-one,[12)] and the structure of *mer*-[V{N(C$_6$H$_5$)C(CH$_3$)CHCOCF$_3$}$_3$] was confirmed by ^{1}H and ^{19}F NMR spectroscopy.[11)] In the present case, tfacH which was freed from **1c** by its reaction with aniline must have reacted with excess aniline to produce the Schiff base, which in turn seems to have replaced the tfac ligand in **1c** to give rise to **11**.

Infrared Spectra. Figure 1 exemplifies the characteristic IR bands of complexes **4d**, **5f**, **7b**, **9r**, and **10i**, all of which contain the hfac anion and 3,5-dimethylaniline as L and are suitable for comparing the IR spectra of complexes of different types. In general complexes **4** and **5** show two or three broad ν(NH) bands of strong to medium intensity in the 3300—3090 cm^{-1} region, while complexes **7** have sharper bands. Complexes **9** show one or two sharp bands of medium to weak intensity in the 3320—3220 cm^{-1} region, which are assigned to the ν(NH) vibration of the bridging anilide ligand. Each of the isolated α and β isomers of **9c** and **9t** shows a single ν(NH) band, of which the frequency is 20—30 cm^{-1} higher for the α form than for the β form. Then other complexes **9** exhibiting two bands in this region seem to be a mixture of both isomers. In the case of complexes **10** containing primary amines as L′, the ν(NH) band from the bridging anilide is indiscernible because of overlapping with the ν(NH) bands from L′. On the other hand, the pyridine complex **10h** shows a sharp band at 3255 cm^{-1}.

The IR bands in the 1800—1500-cm^{-1} region are useful for diagnosing the bonding mode of β-diketonate

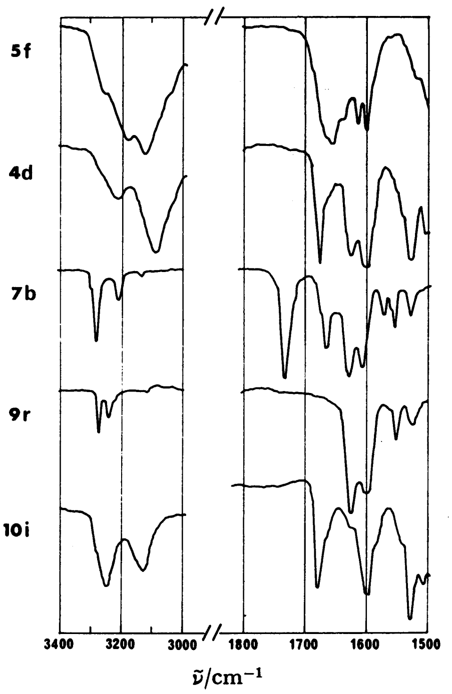


Fig. 1. IR spectra of complexes **5f**, **4d**, **7b**, **9r**, and **10i** in Nujol mull.

anions,[1,2] although aromatic ν(C=C) bands are also observed in this region. The strong absorption of **4d** at 1675 cm^{-1} and a very broad band of **5f** at 1655 cm^{-1} are assigned to the hfac anion in the outer sphere, since these bands are very close to the band exhibited by K(hfac) at 1675 cm^{-1}. Complex **4d** shows additional strong bands caused by the chelating hfac at 1625 and 1526 cm^{-1}. Besides the absorption of chelating hfac at 1628 and 1528 cm^{-1}, complex **7b** exhibits a very strong band at 1733 cm^{-1} which is characteristic of the central-carbon-bonded β-dik ligand.[1,2] The spectrum of **9r** includes the bands caused by the chelating hfac at 1626 and 1526 cm^{-1} but lacks bands in the region higher than 1626 cm^{-1}, certifying absence of hfac either carbon-bonded or situated in the outer sphere. On the other hand, the spectrum of **10i** again demonstrates the existence of hfac in the outer sphere.

NMR Spectra. Solubilities of compounds **4**, **5**, and **7** in organic solvents are generally insufficient to allow NMR measurements and ^{1}H NMR data for only a limited number of compounds were recorded (Table 2). Complexes **4** exhibit two methine signals, of which the lower-field one is assigned to CH of the chelated hfac by reference to the spectrum of [Pt(hfac)-(2-$CH_3C_6H_4NH_2$)$_2$](hfac) showing two methine signals at 5.79 and 6.03 ppm of which the latter is flanked by ^{195}Pt satellites with ^4J(Pt–H) = 8 Hz.[1b] Spectra of **5** are generally broad over the whole field, but three kinds of amine-proton signals are observed inclusive of those from the corresponding **4** and free L, indicating attainment of the following equilibria.

$$\underset{\mathbf{5}}{[PdL_4](hfac)_2} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{4}}{[Pd(hfac)L_2](hfac)} + 2L \tag{1}$$

The same value of about 2×10^{-3} mol^2 dm^{-6} was obtained as K_1 at 25 °C for **5c**, **5e**, and **5f**.

Complex **7c** is not stable either in $CDCl_3$, but signals assignable to **4e** and **1a** are noticed about 1 min after dissolution and grow gradually with time to attain equilibrium (Eq. 2 with 2,4,6-$(CH_3)_3C_6H_2NH_2$ as L), K_2 being estimated as 0.25 at 25 °C. The corresponding platinum(II) complex does not undergo such a disproportionation reaction. The methine proton of the carbon-bonded hfac in **7c** resonates at higher field than that of the chelating hfac and the ^{13}C signal of the methine carbon bonded to the metal also appears at much higher field (33.6 ppm) than that of the chelating hfac (92.0 ppm). The chemical shift of the amine protons in **7c** is also smaller by more than 1 ppm as compared with those in compounds **4** and **5**, indicating absence of the hydrogen-bonding anion in the outer sphere.[1)]

$$\underset{\mathbf{7}}{2[Pd(hfac)(hfac\text{-}C^3)L]} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{4}}{[Pd(hfac)L_2](hfac)} + \underset{\mathbf{1a}}{[Pd(hfac)_2]} \tag{2}$$

Table 3 lists the ^{1}H NMR data for complexes **9**. All complexes except **9h** and **9v** exhibit two sets of signals, demonstrating that they contain stereoisomers α and β. Both the acac methyl protons and the anilide proton of **9c**-α resonate at higher field than those of **9c**-β. Thus the higher-field one of the two NH signals from each complex was assigned to the α form by reference to **9c**. Then the hfac methine signals from **9m**—**9u** were distinguished based on the area ratio to accord with that of the NH signals. In each case the hfac methine proton of the α form resonates at higher field than that of the β form, although the chemical shifts

Table 2. ^{1}H NMR data for [Pd(hfac)L_2](hfac) (**4**), [PdL_4](hfac)$_2$ (**5**), and [Pd(hfac)(hfac-C^3)L] (**7**) in $CDCl_3$ at room temperature[a)]

Compd	CH of hfac[b)]		L		
	Chelated	OS or C-Bonded	NH_2	CH_3[c)]	Ring CH
4d	6.10	6.01	6.8	2.25(3,5)	6.82 br
4e	5.99	5.81	6.2_8	2.49(2,6), 2.16(4)	6.81
5c		5.98 br	5.8	2.20(4)	7.03 br
5e		5.90 br	5.4	2.21 br (2,5)	6.95 br
5f		5.93 br	6.1	2.16(3,5)	6.63 br
7c	6.12	5.31	4.3_4	2.18(2,4,6)	6.80

a) Chemical shift is expressed in ppm from internal Me_4Si, br: broad. b) OS abbreviates the outer sphere. c) Figures in parentheses give the positions of substitution on the phenyl ring.

TABLE 3. ^{1}H NMR DATA FOR $[Pd(\beta\text{-dik})(L-H)]_2$ (**9**) IN $CDCl_3$ AT ROOM TEMPERATURE[a)]

Compd	[α]/[β]	β-Dik		Anilide (L-H)		
		CH_3	CH	NH	CH_3	Ring CH
9c-α		1.58	5.07	1.1_8	2.35, 2.42	$H^{3,4}$ 6.74, H^6 8.61
9c-β		1.65	5.07	1.3_1	2.42, 2.51	$H^{3,4}$ 6.74, H^6 8.28
9h[b)]		1.67	5.67			6—7 m
9i[c)]		1.75, 1.83	5.46	1.2		7.0 m, 7.7 m
9m α	3—4		5.90	1.0_3		7.2 m, 7.9 m
9m β	1		5.95	1.2_5		
9n α	2		5.87	1.1_5	2.35	7.1 m, 8.7 m
9n β	3		5.91	1.3_6	2.39	
9o α	*ca.* 4		5.90	0.9_8	2.22	$H^{2,6}$ 7.79 d (J=8 Hz), $H^{3,5}$ 6.99
9o β	3		5.94	1.2_4		
9p α	1		5.88	1.1_5	2.28, 2.42	$H^{3,4}$ 6.8 m, H^6 8.37
9p β	2		5.92	1.3_5	2.34, 2.47	$H^{3,4}$ 6.8 m, H^6 8.47
9r α	1		5.94	0.9_8	2.32	7.49 br, 6.79 br
9r β	1		5.95	1.2_2		
9u α	3—4		5.95	4.6_3		H^3 8.0_4 dd (J=8.2 Hz), $H^{4,5}$ 7.1—7.8 m H^6 9.01 d, br (J=8 Hz) for α H^6 9.28 dd (J=8.2 Hz) for β
9u β	1		5.98	4.9_1		
9v			6.00	$1._5$		$H^{2,6}$, $H^{3,5}$ 8.10, 7.95 (AB quartet, J=9 Hz)

a) Same as footnote a) for Table 2, m=multiplet, d=doublet, dd=doublet of doublets. b) In C_6D_6. c) In CD_2Cl_2.

TABLE 4. $^{13}C\{^1H\}$ NMR DATA FOR COMPLEXES **9** IN $CDCl_3$ AT ROOM TEMPERATURE[a)]

Compd	β-Dik[b)]			Anilide[c)]						
	CH_3 or CF_3	CO	CH	C^1	C^2	C^3	C^4	C^5	C^6	CH_3
9c-α	25.9	185.6	100.0	149.2	128.0	129.0	122.6	135.2	125.8	18.4(2), 21.2(5)
9c-β	25.9	185.6	100.0	149.6	127.2	129.7	122.6	135.6	125.0	18.5(2), 21.2(5)
9m α	116.1	174.4	91.6	147.3	124.1	128.9	124.4			
9m β	[286]	[36]		d)	123.7	128.5	124.4			
9n α	116.1	174.4	91.5	145.4	d)	130.0	124.2	126.6	124.9	18.0(2)
9n β	[284]	[36]		146.8	d)	130.7	124.3	127.0	124.1	18.0(2)
9o α	116.2	174.4	91.5	145.2	123.5	129.5	134.0			21.0(4)
9o β	[284]	[36]		144.6	124.0	129.1	134.0			21.0(4)
9r α	116.2	174.4	91.6	147.0	122.1	138.3	126.2			21.0(3, 5)
9r β	[284]	[35]		147.5	121.6	138.6	126.2			21.0(3, 5)

a,c) Same as footnotes a) and c) for Table 2. b) Figures in brackets give the J(C–F) values in Hz. d) Indiscernible because of overlapping with other signals or low intensity.

were accidentally same for acac methine protons of **9c**-α and **9c**-β. The abundance ratio of isomers for each complex determined by the ^{1}H NMR measurements parallels the relative intensities of the ν(NH) bands in the IR spectrum.

Very recently a single crystal of $[AlMe_2(i\text{-}PrNH)]_2$ was revealed by X-ray analysis to contain two stereoisomers in the ratio of 2 : 1, of which both have four-membered $(AlN)_2$ rings.[13)] The syn to anti ratio of 2 : 1 was preserved in toluene solution and changed only slightly with temperature. In the case of $[AlBr(Et)(t\text{-}BuNH)]_2$, five stereoisomers are conceivable, of which two were isolated and shown to isomerize in benzene solution at room temperature to give an equilibrium mixture containing three principal isomers.[14)] In the case of the present palladium(II) complexes, the stereoisomers are very inert in solution. Even when heated to 60 °C for several hours, **9c**-α in $CDCl_3$ solution showed no sign of isomerization to **9c**-β. The isomer ratios of other compounds **9** do not change with temperature either. Transformation between the syn and anti forms either by cleavage of the anilide bridge or by dissociation of the anilide proton does not occur easily, and the isomer ratio observed is not an equilibrium value in solution, but was realized under the preparative conditions.

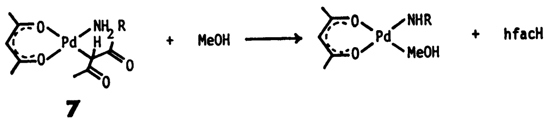
The ^{19}F NMR spectrum of **9n** in dichloromethane at room temperature exhibits two signals at 3.36 and 3.06 ppm downfield from external CF_3COOH. The area ratio (2 : 3) coincides with the isomer ratio determined by ^{1}H NMR spectroscopy. Therefore the two ^{19}F signals are assigned to the α and β forms, respectively.

As is seen in Table 3, the NH proton of the anilide ligand in complexes **9** resonates usually in the field higher than 1.5 ppm, but that of **9u** absorbs in remarkably lower field. This exceptional behavior may stem from the hydrogen bonding of the NH group to the ortho nitro group, the NH group being retained on the same plane as the phenyl ring and suffering its anisotropic effect.

The ^{13}C NMR spectra of complexes **4**, **5**, and **7** are similar to those for corresponding β-dik complexes containing other nitrogen bases as L.[1)] Therefore ^{13}C{^{1}H} NMR data only for the new type complexes **9** are listed in Table 4. In each case two sets of signals from the phenyl-ring carbons are observed and assigned to α and β forms based on the relative intensities to accord with the isomer ratios determined by ^{1}H NMR measurements. Shieldings of the β-diketonate carbons in **9** are quite similar to those of the corresponding bis-chelates **1**[4b)] and chelating ligands in **4** and **7** containing alkylamines as L.[1a)] Signals of the β-dik carbons do not show any difference due to the stereoisomerism, suggesting that the splitting observed for proton signals may be caused by different anisotropic effect exerted through space and not through bonds by the phenyl rings of bridging anilide ligands in the syn and anti isomers. Complexes **10** are not sufficiently soluble in usual solvents to allow NMR measurements.

Relative Stabilities of Complexes. Relative stabilities of the palladium(II) complexes **4**, **5**, and **7** containing ammonia, alkylamines, and pyridines as L were found to depend on basicities of both the nitrogen bases and β-dik anions as well as bulkiness of the former.[1a)] Thus complexes **5** are favored by more basic L and less basic β-dik. Anilines are far less basic than alkylamines and pyridines, and can not displace the β-dik ligands in [Pd(acac)$_2$] (**1b**), [Pd(bzac)$_2$], and [Pd(tfac)$_2$] (**1c**), reacting only with [Pd(hfac)$_2$] (**1a**) to produce complexes **4**, **5**, and **7**. It is noteworthy that reactions between anilines and **1a** afford either **4** or **5** depending on the reactants mole ratio, whereas primary alkylamines and pyridine gave solely **5**[1a)] because of higher reactivity of [Pd(hfac)L$_2$](hfac) toward L than that of **1a** when L are these bases. 2-Nitro- and 4-nitroanilines, which are less basic than aniline, the pK_a values of conjugate acids being -0.26 and 1.11 as compared with 4.60 for aniline,[15)] do not give **4** and **5**, but produce anilide complexes **9**. On the other hand, 2-methyl- and 2,4-dimethylanilines are more basic than aniline, giving **4** and **5**. It may be due to their bulkiness that 2,6-dimethyl- and 2,4,6-trimethylanilines produce **4** and **7** but do not give **5**. The central-carbon-bonded complexes **7** were supposed to be preferred by β-diketones which favor the keto form over enol.[1,16)] In spite of the fact that hfacH is composed exclusively of the enol tautomer,[17)] some substituted anilines give rise to complexes **7**. Besides the basicity at the central carbon atom of β-dik anion (the keto-favoring factor), some balance between basicities of L and β-dik might be important for stabilization of **7**.

Mechanism for Formation of the Anilide-bridged Complexes. Kinetic and equilibrium studies on the reactions of **1b** with alkylamines revealed that complexes of type **7** are produced not directly from **1b** but *via* **4** reversibly, and the equilibrium is favorable to **7** in dichloromethane and to **4** in methanol when diethylamine is used as L.[18)] The same situation will be reallized for the present aniline complexes. Complexes **7a**—**7c** were prepared in benzene and changed spontaneously to complexes **9** in methanol. The transformation reaction might be represented by Eqs. 3 and 4.



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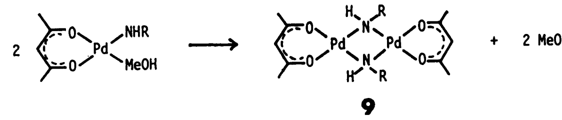
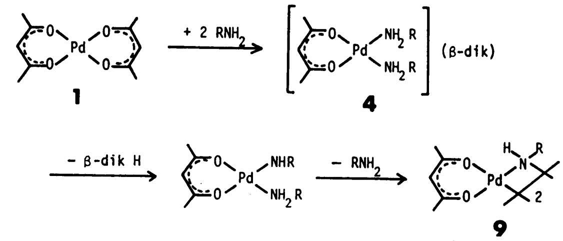
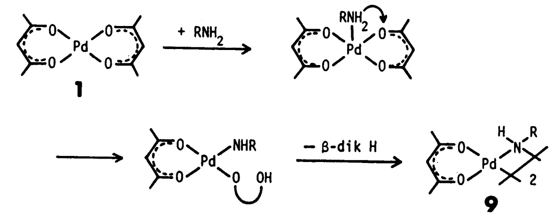


(4)

It is a characteristic feature of anilines to afford anilide complexes **9** irreversibly by the reactions with **1** on heating. The overall reaction might proceed *via* complex **4** (Eq. 5) or alternatively in a direct fashion as depicted in Eq. 6. In previous papers,[1a,19)] complexes **4** and **5** containing secondary and primary amines as L, respectively, were reported to catalyze the hydrogen exchange reactions between amines and chloroform. Deprotonation of the coordinated amine molecule by the β-dik anion in the outer sphere was presumed to be a key step and the rate was found to parallel the basicity of the β-dik anion. The present results that the reactions of [Pd(β-dik)$_2$] (β-dik=acac, bzac, and tfac) with aniline and its methyl derivatives as well as reactions of **1a** with nitroanilines do not afford complexes **4** but give rise directly to **9** seem to support reaction scheme 6.



(5)



(6)

1,8-Bis(dimethylamino)naphthalene, a powerful proton acceptor known as "proton sponge," greatly accelerates the **9**-forming reactions. An equimolar mixture of **1a** and 4-methylaniline in CDCl$_3$ promptly attains an equilibrium shown by Eq. 2, K_2 being estimated as 0.1 from ^{1}H NMR spectroscopy. On addition of an equimolar amount of "proton sponge" to this mixture, the reaction to form **9o** proceeds almost quantitatively at room temperature and **9o** and the hfac salt **12** were isolated in 88 and 27% yields, respectively. An equimolar mixture of **1a** and 2-nitroaniline in CDCl$_3$ showed no sign of reaction on the NMR spectra after a while at room temperature, but reacted immediately on addition of the equimolar base to result in **9u** and **12** quantitatively (based on the ^{1}H and ^{13}C NMR spectra), which were isolated in 60 and 48% yields, respectively.

These results demonstrate that the deprotonation of anilines is the most important step in production of **9**. In the absence of added base, basicity of the β-dik anion and acidity of the amine seem to be the most important factors to facilitate formation of the anilide complexes. Much lower acidities of alkylamines as compared with those of anilines may be the reason why alkylamines fail to afford amide complexes.

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