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PREPARATIONS AND CHARACTERIZATION OF NEW 2-FURFURYLPALLADIUM(II) COMPLEXES

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Summary

2-Furfuryl chloride reacted with $[Pd(PPh_3)_4]$ to give $[Pd(\eta^1\text{-}CH_2Fu)Cl(PPh_3)_2]$ (Fu = 2-furyl) (I) and with bis(dibenzylideneacetone)palladium(0) in the presence of the appropriate amount of PPh_3 or 4-picoline to afford $[Pd(\eta^3\text{-}CH_2Fu)Cl(PPh_3)]$ or $[Pd(\eta^1\text{-}CH_2Fu)Cl(4\text{-picoline})_2]$, respectively. Complex I was treated with Tl(acac), $AgClO_4$, and $Na[BPz_3R]$ (Pz = 1-pyrazolyl, R = H or Pz) to give $[Pd(\eta^1\text{-}CH_2Fu)(acac)(PPh_3)]$, $[Pd(\eta^3\text{-}CH_2Fu)(PPh_3)_2]ClO_4$, and $[Pd(\eta^1\text{-}CH_2Fu)(BPz_3R)(PPh_3)]$, respectively. These new 2-furfurylpalladium(II) complexes were characterized on the basis of elemental analysis, electric conductivity, and spectroscopic data.

Introduction

The coordination behavior of heteroaromatic groups to transition metals has been investigated [1,2] in connection with benzyl-transition metal complexes [3—5]. Thenyl groups were reported to show either η^1- or η^3-type coordination to molybdenum and iron [1]. Furthermore, it has been reported that 2-picolyl complexes have either a mononuclear σ-bonded structure or a dinuclear structure involving coordination of the methylene carbon and 1-nitrogen atoms [2]. However, little is known about the coordination behavior of the furfuryl group.

This paper deals with new chloro-2-furfurylpalladium(II) complexes, which were prepared by reactions of 2-furfuryl chloride with tetrakis(triphenylphosphine)palladium(0), $[Pd(PPh_3)_4]$, or bis(dibenzylideneacetone)palladium(0), $[Pd(dba)_2]$ (dba = dibenzylideneacetone), and with some derivatives of one of the chloro-2-furfurylpalladium(II) complexes. The coordination behavior of the 2-furfuryl group is discussed.

Experimental

General procedures

Melting points and molar conductivities were measured, and IR and ^{1}H NMR spectra were run according to the methods described in the previous paper [2]. 2-Furfuryl chloride [6], [Pd(PPh$_3$)$_4$] [7], [Pd(dba)$_2$] [8], thallium(I) acetylacetonate, [Tl(acac)], [9], and sodium poly(1-pyrazolyl)borates Na[BHPz$_3$] (Pz = 1-pyrazolyl) and Na[BPz$_4$] [10] were prepared by literature methods. Solvents were dried by standard methods and distilled. All preparative operations were performed under an atmosphere of dry nitrogen.

Reaction of [Pd(PPh$_3$)$_4$] with 2-furfuryl chloride

A benzene suspension (65 ml) containing [Pd(PPh$_3$)$_4$] (1.3 mmol) and 2-furfuryl chloride (22.2 mmol) was stirred at room temperature for 14 h. After the reaction mixture had been evaporated to dryness, the residue was recrystallized from dichloromethane/diethyl ether to give [PdCl(η^1-CH$_2$Fu)(PPh$_3$)$_2$] (Fu = 2-furyl) (I).

Reactions of [Pd(dba)$_2$] with 2-furfuryl chloride in the presence of Lewis bases

Triphenylphosphine (0.70 mmol) was added to a THF suspension (22.5 ml) containing [Pd(dba)$_2$] (0.70 mmol) and 2-furfuryl chloride (1.32 mmol). The mixture was stirred at room temperature for 25 min, and was concentrated and diluted with petroleum ether to yield a yellow precipitate. The precipitate was recrystallized from dichloromethane and diethyl ether to yield [Pd(η^3-CH$_2$Fu)-Cl(PPh$_3$)] (II).

2-Furfuryl chloride (0.64 mmol) and [Pd(dba)$_2$] (0.52 mmol) reacted similarly in the presence of 4-picoline (pic) (1.04 mmol) to yield [Pd(η^1-CH$_2$Fu)Cl(pic)$_2$] (III).

Reactions of I with Tl(acac) and silver perchlorate

A benzene suspension (60 ml) of I (0.63 mmol) and Tl(acac) (0.63 mmol) was stirred at room temperature for 4 h. After filtration, the filtrate was evaporated in vacuo. The residue was washed with diethyl ether to afford a yellow powder, [Pd(η^1-CH$_2$Fu)(acac)(PPh$_3$)] (IV).

Complex I reacted similarly with silver perchlorate, followed by recrystallization from dichloromethane/hexane, to yield pale yellow olive needles, [Pd(η^3-CH$_2$Fu)(PPh$_3$)$_2$]ClO$_4$ (V).

Reactions of I with sodium poly(1-pyrazolyl)borates

A benzene suspension (45 ml) of I (0.27 mmol) and Na[BHPz$_3$] (0.34 mmol) was heated at 50°C for 1 h. After filtration, the filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane/hexane to give a pale yellow powder, [Pd(η^1-CH$_2$Fu)(BHPz$_3$)(PPh$_3$)] (VI).

Similarly, complex I reacted with Na[BPz$_4$] in benzene at 50°C for 5 h, followed by similar procedures as above, to yield [Pd(η^1-CH$_2$Fu)(BPz$_4$)(PPh$_3$)] (VII).

Results and discussion

Oxidative addition of 2-furfuryl chloride to [Pd(PPh$_3$)$_4$] afforded a η^1-2-furfurylpalladium(II) complex, I. Bis(dibenzylideneacetone)palladium(0) reacted with 2-furfuryl chloride in the presence of an equimolar amount of PPh$_3$ and 4-picoline to give II in 40% yield and III in 27% yield, respectively. The presence of two molar equivalents of 4-picoline increased the yield of III to 64%. Complex I was treated with Tl(acac), AgClO$_4$, Na[BHPz$_3$], and Na[BPz$_4$] to yield the corresponding 2-furfuryl-palladium(II) complexes, IV—VII, respectively. Complexes I—VII are stable in the solid state in air. Yields, elemental analyses, and some properties of these new palladium complexes are given in Tables 1 and 2.

Complexes I, II, and IV—VII, each showed two bands near 1430 and 1470 cm^{-1}, attributable to PPh$_3$. Complex I, III, and V showed two weak or medium bands near 1490 and 1385 cm^{-1} (Table 2), characteristic of the 2-furfuryl group [11]. However, in the case of the IR spectra of IV, VI, and VII, these two bands could not be distinguished owing to overlapping with neighboring strong bands. The molecular weight of II, measured by vapor pressure osmometry in benzene, was 488 (Calcd.: 485), indicating a mononuclear structure.

η^1-Furfuryl complexes I, III, IV, VI, and VII

The ^{1}H NMR spectra of I, III, IV, and VI exhibited three double doublets near δ 5.0—5.9 (1 H), 5.9—6.1 (1 H), and 6.8—7.3 ppm (1 H) [$^3J(3, 4)$ = ca. 3.2 Hz, $^4J(3, 5)$ = 1.0 Hz, and $^3J(4, 5)$ 2 Hz], characteristic of the 2-furfuryl group (Table 3). Complexes I and III showed singlets at δ 2.54 and 2.77 ppm (each, 2 H), respectively, which were assignable to the methylene protons of the 2-furfuryl group, indicating that the methylene carbon was σ-bonded to the palladium atom.

The methylene protons in I show no coupling to the ^{31}P atom of the PPh$_3$ ligands, confirming the *trans* configuration of I. Since complexes IV, VI, and VII have a bidentate chelating ligand, they involve a σ-bonded 2-furfuryl group, situated *cis* to the PPh$_3$ ligand. The methylene protons of the 2-furfuryl group in these complexes coupled to the ^{31}P atom of the PPh$_3$ ligand with a coupling constant of about 4.5 Hz.

TABLE 1

YIELDS AND ANALYTICAL DATA

Complex [a]	Yield (%)	M.p. [b] (°C)	Found (calc) (%)		
			C	H	N
I	87	130—134 [c]	66.31(65.87)	4.70(4.72)	—
II	40	154—158	57.27(56.93)	4.15(4.15)	—
III	64	104—115	49.44(49.90)	4.54(4.67)	6.70(6.85)
IV	73	144—160 [c]	61.56(61.27)	4.84(4.96)	—
V	57	120—189 [c]	60.87(60.68)	4.40(4.35)	—
VI	31	148—151 [c]	57.93(57.99)	4.57(4.56)	12.46(12.68)
VII	35	171—174 [c]	57.46(57.68)	4.45(4.43)	15.40(15.37)

[a] The color of I—III, VI, and VII is pale yellow. [b] All melting points are uncorrected. [c] With decomposition.

TABLE 2

IR DATA AND MOLAR CONDUCTIVITIES OF THE PALLADIUM(II) COMPLEXES

Complex	IR data [a]			Conductivity [h] Ω^{-1} cm^2 mol^{-1}
	ν(C=C) + ν(C—O) [b]		Others [c]	
I	1487w,	1384w	268[ν(Pd—Cl)]	—
III	1500m,	1380w	1615s + 1560w[ν(C=N) + ν(C=C)] [d], 263[ν(Pd—Cl)]	—
IV	— [e]	— [f]	1572s + 1502s + 1383s[ν(C=O) + ν(C=C)]	0.24
V	1490m,	1392m	1100s[ν(Cl—O)]	112
VI	— [e]	— [f]	2432s[ν(B—H)], 1492s + 1392s + 1382sh[ν(C=C) + ν(C=N)] [g]	0.49
VII	— [e]	— [f]	1486s + 1410s + 1392s[ν(C=C) + ν(C=N)] [g]	1.0

[a] In cm^{-1}, in KBr disk. [b] Due to the 2-furfuryl group. [c] Assignment is given in parentheses. [d] Due to the pyridine ring. [e] Obscured by a band near 1495 cm^{-1}. [f] Obscured by a band near 1390 cm^{-1}. [g] Due to the pyrazole group [12]. [h] In 1.0×10^{-3} *M* acetone solution.

The ^{1}H NMR spectrum of IV at 20° C showed a slightly broad singlet at δ 1.83 ppm (6 H), assignable to two methyl groups of the acac moiety. The singlet broadened at 2° C and turned into two sharp singlets at δ 1.66 and 2.00 ppm (each, 3 H) at —20° C. The broadening of these signals was ascribed to rapid exchange between the two methyl groups above 2° C, owing to the strong *trans* influence of the 2-furfuryl group and the PPh_3 ligand *trans* to two acac-oxygen atoms [2].

The ^{1}H NMR spectrum of VI showed a triplet (3 H) at δ 6.08 ppm and two doublets at δ 7.19 (3 H) and 7.63 ppm (3 H), characteristic of the 1-pyrazolyl

TABLE 3

^{1}H NMR DATA OF THE PALLADIUM(II) COMPLEXES [a]

Complex	2-Furfuryl group				Others [c]
	CH_2	3-H	4-H	5-H	
I	2.54(s)	5.30(dd) [b]	5.96(dd) [b]	7.16(dd) [b]	—
II	2.71(s) [d]	6.27(dd) [e]	6.63(b)	— [f]	—
III	2.77(s)	5.53(dd) [b]	6.11(dd) [b]	7.25(dd) [b]	2.37(s, 6 H, Me of pic) 7.10(d, 4 H, 3-H of pic) 8.65(d, 4 H, 2-H of pic)
IV	2.63(d) [g]	5.86(dd) [b]	6.10(dd) [b]	7.18(dd) [b]	1.83(s, 6 H, Me) [d] 5.25(s, 1 H, CH)
V [h]	3.03(dd) [i,j] 3.72(d) [i]	6.06(dd) [e]	5.16(b, d)	— [f]	—
VI	2.60(d) [g]	5.06(dd) [b]	6.00(dd) [b]	6.87(dd) [b]	6.08(t, 3 H, 4-H of Pz) [k] 7.19(d, 3 H, 3-H of Pz) [k] 7.63(d, 3 H, 5-H of Pz) [k]
VII	2.49(d) [g]	5.07(dd) [b]	5.97(dd) [b]	— [f]	6.03(b, 4 H, 4-H of Pz) [d] 7.06(b, 4 H, 3-H of Pz) [d] 7.74(b, 5-H of Pz) [d]

[a] δ value in ppm from TMS at 20° C. In $CDCl_3$, except for V. Abbreviations used: b = broad, d = doublet, dd = double doublet, s = singlet and t = triplet. Phenyl protons are omitted. [b] $^3J(2, 4)$ = ca. 3.2 Hz, $^4J(3, 5)$ = 1.0 Hz and $^3J(4, 5)$ = ca. 2 Hz. [c] Proton number and the assignment are given in parentheses. [d] See the text. [e] $^3J(PH)$ = ca. 8 Hz, $^3J(3, 4)$ = 3.2 Hz. [f] Obscured by the phenyl protons. [g] $^3J(HP)$ = ca. 4.5 Hz. [h] In CD_2Cl_2. [i] $^2J(H_AH_B)$ = 6.0 Hz. [j] $^3J(HP)$ = 11.3 Hz. [k] $^3J(3, 4)$ and $^3J(4, 5)$ are virtually 2.1 Hz.

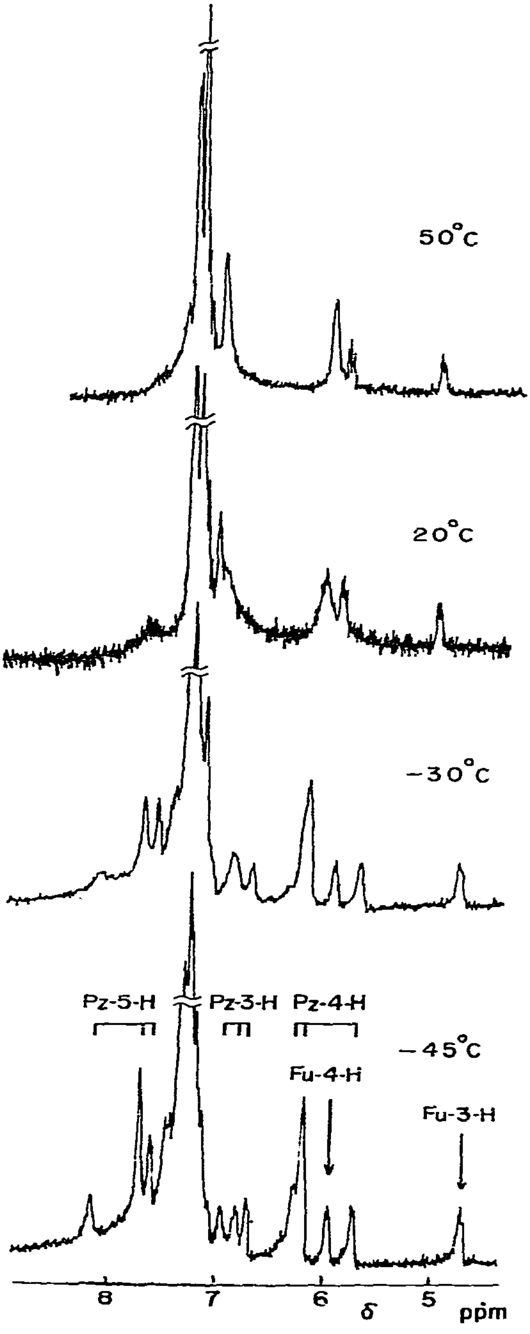
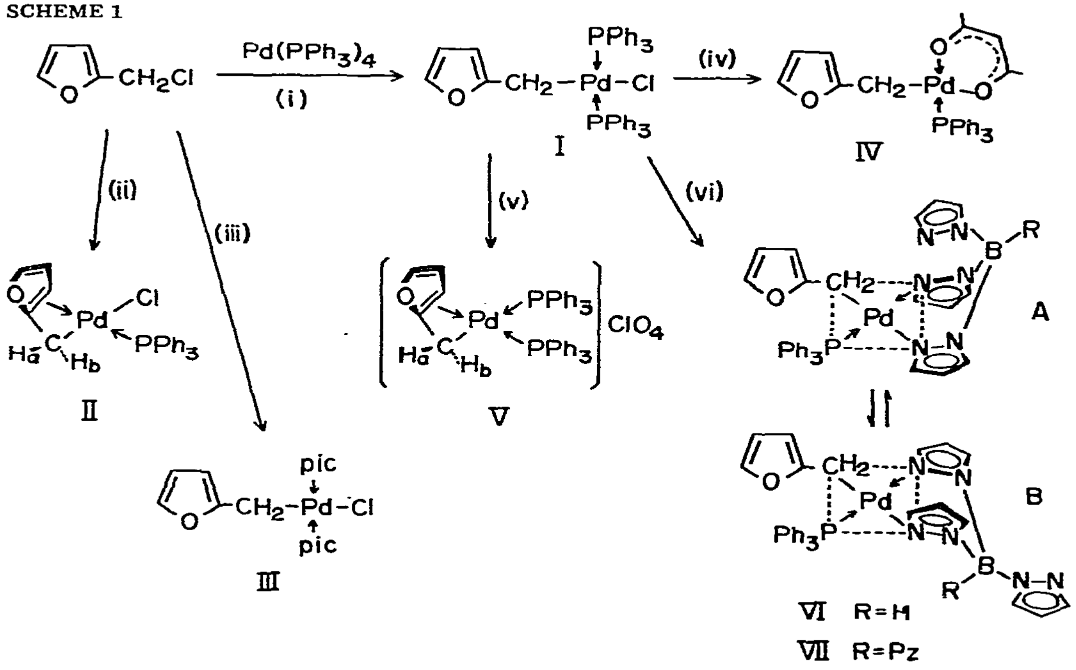


Fig. 1. Low field regions of ^1H NMR spectra of VII in $CDCl_3$.

protons (Table 3). This indicates that the three 1-pyrazolyl groups in VI are spectroscopically equivalent at room temperature, exchanging with each other rapidly on the NMR time scale [13]. The triplet and the two doublets, each turned into a slightly broad signal at −35° C, indicating that the exchanging motion of the three pyrazolyl groups became fairly sluggish at this temperature. However, no slow exchange-limiting spectrum was obtained.

The ^{1}H NMR spectrum of VII at 50° C exhibited two fairly sharp signals (each intensity is 4 H) near δ 6.03 and 7.06 ppm, assignable to the 1-pyrazolyl 4-H's and 3-H's, respectively, implying a fairly rapid exchange among the four 1-pyrazolyl groups *. On cooling at 20° C, these signals broadened remarkably (Table 3). At —30° C, the signal at δ 7.06 ppm separated into two signals at δ 6.70 (1 H) and 6.86 (2 H) ppm (Fig. 1). The fourth 3-H signal (1 H) seemed to overlap with the phenyl and furfuryl 5-H protons. At —45° C, the larger signal at δ 6.86 ppm turned into two signals at δ 6.76 (1 H) and 6.90 (1 H) ppm. The signal at δ 6.03 ppm (for 4-H's) also changed, corresponding to the 3-H signals. These data indicate that the fluxional motion of the BPz$_4$ ligand was actually quenched near —45° C. At 20° C, the 2-furfuryl methylene protons resonated as a doublet at δ 2.49 ppm [2 H, ^3J(HP) = 4.8 Hz], which coalesced into a broad signal at 0° C and turned into slightly broad AB type quartet [$\Delta\delta$ = 0.45 ppm, ^2J(HH) = ca. 8 Hz] at —45° C, indicating the non-equivalence of the two methylene protons. This was possibly attributed both to a restricted rotation of the 2-furfuryl—palladium σ-bond due to the bulky PPh$_3$ and BPz$_4$ ligands, and to quenching of the fluxional motion between two conformations of the BPz$_4$ ligand (VII A and B in Scheme 1).

SCHEME 1



i) In benzene; ii) [Pd(dba)$_2$] + PPh$_3$; iii) [Pd(dba)$_2$] + 4 picoline; iv) Tl(acac); v) AgClO$_4$; vi) Na[BPz$_3$R] (R = H or Pz).

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* At 50°C, the 5-H of the pyrazole groups could not be distinguished, probably owing to overlapping with the phenyl protons.

η^3-Furfuryl complexes, II and V

The ^{1}H NMR spectrum of the cationic 2-furfuryl complex V exhibited a double doublet at δ 3.03 ppm [1 H, $^2J(H_AH_B) = 6.0$ Hz and $^3J(H_AP) = 11.3$ Hz] and a doublet at δ 3.72 ppm (1 H). These two signals were assigned to two non-equivalent protons of the methylene group. Moreover, the 3-H proton of the 2-furfuryl group coupled to the ^{31}P atom of the PPh_3 ligand besides couplings to 4-H. On the basis of these observations, the 2-furfuryl group in V was associated with a rigid $^3\eta$-type coordination to the palladium atom.

Since the neutral complex, II, has the 2-furfuryl group and one mole of PPh_3, the 2-furfuryl group was believed to be of the η^3-type. The ^{1}H NMR spectrum showed a sharp singlet at δ 2.71 ppm (2 H) above −13° C. The singlet broadened at −37° C and changed into a very broad hump at −55° C. These facts imply that the two methylene protons of the η^3-2-furfuryl group exchange rapidly on the NMR time scale above −55° C. This is in contrast with the rigid coordination of the η^3-2-furfuryl group in V. The positive charge of the central metal in V is probably responsible for the rigid coordination of the η^3-2-furfuryl group.

Conclusions

The 2-furfuryl group gave stable η^1- or η^3-2-furfurylpalladium(II) complexes. Such coordination behavior of the 2-furfuryl group is very similar to those of benzyl [3—5] and thenyl groups [1].

Chloro(η^1-2-furfuryl)di(4-picoline)palladium(II), III, reacted with $AgClO_4$ to yield palladium black, without the formation of a cationic η^3-2-furfuryl type complex, in sharp contrast to the case of I. It seems likely that 4-picoline is unable to stabilize the η^3-2-furfuryl-palladium(II) bond, owing to its poor π-accepting character. Furfuryl chloride reacted with $[Pd(dba)_2]$ either at room temperature or at 50° C in the absence of a Lewis base such as PPh_3 or 4-picoline, to form palladium black without the isolation of $[\{Pd(\eta^3\text{-}CH_2Fu)Cl\}_2]$. The η^3-2-furfuryl—palladium(II) bond probably needs a ligand having appropriate σ-donating and π-accepting character, as found in a tertiary phosphine.

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