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Synthesis of Cyclopalladated Acetylhydrazones of *p*-Methylacetophenone, Acetylferrocene and 2-Acetylthiophene

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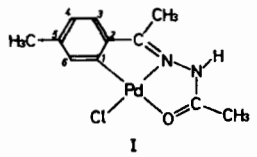
Acetylhydrazones of p-*methylacetophenone, acetylferrocene, and 2-acetylthiophene (HL) are easily cyclopalladated to give the complexes [PdClL]. A palladium–carbon bond is formed with the* ortho *positions of phenyl and ferrocenyl rings and with the position 3 of a thienyl ring. The complexes react with pyridine (py) to give the adducts [PdClL(py)] which have a* trans-*N,N and* trans-*C,Cl arrangement. Some bromo analogues are also prepared and characterized.*

Introduction

Acetylhydrazones derived from condensation of acylhydrazine with organic carbonyl compounds, R^1–CONH–N=CR^2R^3. are coordinated to transition metal ions through acyl-oxygen and imino-nitrogen atoms [1–4]. It is interesting that the acylhydrazones can act as either neutral or anionic ligands depending upon the acidity of solutions from which complexes are obtained and the deprotonation of the coordinated acylhydrazones occurs at the amide group (–CONH–) [1–4]. We have, therefore, examined palladium(II) complexes of the acetylhydrazones (HL) of *p*-methylacetophenone (abbreviated as Hpma), acetylferrocene (Hafa), and acetylthiophene (Hata) and found that a palladium(II)–carbon bond is formed in the complexes (Structures I, II, and III). In this case deprotonation occurs, however, at an aromatic ring and an acid amide group remains protonated. Cyclopalladation of thiophene rings is remarkable, since only one example is, so far, known for 2-(2-thienyl)pyridine [5]. 2-Substituted thiophene rings undergo usually electrophilic substitution reactions at position 5 [6], but cyclopalladation occurs at position 3. The driving force may be provided by chelation of the acetylhydrazone group to palladium(II). Preliminary results of this investigation have been reported [7].



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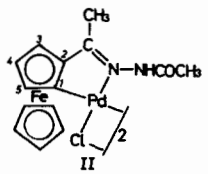

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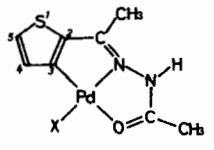


III

Experimental

Preparation of the Acetylhydrazones (HL)

A mixture of 0.74 g of acetylhydrazine, 1.26 g of 2-acetylthiophene, and 0.1 ml of acetic acid in 20 ml of ethanol was heated on a steam bath for 1 h and cooled to room temperature. The crystals precipitated were washed with ethanol and dried in air. The other two acetylhydrazones were similarly prepared. The yields, melting points, and analytical data are shown in Table I.

Preparation of the Complexes [PdClL]

To a stirred solution of lithium tetrachloropalladate in 40 ml of methanol, prepared *in situ* from 177 mg of palladium(II) chloride and 100 mg of lithium chloride, was added 1 mmol of acetylhydrazone and then 136 mg of sodium acetate hydrate. The mixture was stirred for 2 days at room temperature. The precipitate was washed with methanol and dried in air. The bromo analogues were prepared by using excess lithium bromide instead of lithium chloride. The yields and analytical data are summarized in Table I. Some of these complexes are reported in a preliminary communication [7].

Preparation of the Complexes [PdClL(py)]

To a suspension of 1 mmol of [PdClL] in 20 ml of dichloromethane was added three fold excess of pyridine (py) and the mixture was stirred until the clear solution had been obtained. The reaction mixture was filtered, mixed with 20 ml of n-hexane,

TABLE I. Colors, Melting Points, Yields, and Analytical Data for the Ligands and Complexes.

Compound	Color	M.P. (°C)	Yield (%)	Analysis, found (calcd.)		
				C%	H%	N%
Hpma	White	165–166	78	69.2 (69.5)	7.4 (7.4)	14.7 (14.7)
[PdCl(pma)]	Light yellow	215(dec)[a]	79	39.7 (39.9)	4.0 (4.0)	7.8[b] (8.4)
[PdBr(pma)]	Yellow	205(dec)	80	35.7 (35.2)	3.5 (3.5)	7.6 (7.5)
[PdCl(pma)py]	Light yellow	200(dec)	63	46.7 (46.8)	4.3 (4.4)	10.1 (10.2)
Hafa	Brown	167–168	77	58.7 (59.2)	5.5 (5.6)	9.7 (9.9)
[PdCl(afa)]	Reddish brown	190(dec)	79	39.6 (39.6)	3.5 (3.6)	6.4[b] (6.6)
[PdBr(afa)]	Reddish brown	190(dec)	77	35.8 (36.1)	3.0 (3.2)	5.9 (6.0)
[PdCl(afa)py]	Red	195(dec)	72	45.4 (45.3)	3.7 (4.0)	7.8 (8.3)
Hata	Light yellow	163–164	42	52.3 (52.7)	5.4 (5.5)	15.1 (15.4)
[PdCl(ata)]	Brown	225(dec)	70	29.5 (29.7)	3.1 (2.8)	7.8[b] (8.7)
[PdBr(ata)]	Brown	215(dec)	57	27.0 (26.2)	2.6 (2.5)	7.5[b] (7.6)
[PdCl(ata)py]	Yellow	171–173	40	38.7 (38.8)	3.2 (3.5)	10.1 (10.4)
[PdBr(ata)py]	Orange	173(dec)	20	34.5 (35.0)	2.8 (3.2)	9.1 (9.4)
[PdCl(ata)PBu_3]	Yellow	132–133	27	45.7 (45.7)	7.2 (6.9)	5.3 (5.3)

[a]dec = decomposition. [b]These complexes have been reported previously [7].

and concentrated to a small volume to form crystals. [PdBr(ata)py] was similarly prepared from [PdBr(ata)] and [PdCl(ata)PBu_3] by using stoichiometric amount of tri-n-butylphosphine(PBu_3).

Measurements

The methods of measurements were previously reported [8].

Results and Discussion

Reactions of lithium tetrahalopalladate with acetylhydrazones (HL) in the presence of sodium acetate yield the complexes [PdXL] (X = Cl, Br) (Table I). All the infrared spectra of [PdXL] (Table II) show ν(NH) between 3150 and 3450 cm^{-1} suggesting that the hydrogen atom of the acid amide group (–CONH–) is not lost. The presence of the N–H group is also supported by the PMR spectra which show a broad signal at a low field and the signal disappears upon addition of D_2O. The methyl resonances are observed as singlets in the normal region.

The PMR spectrum of Hpma shows two doublets due to a phenyl ring and the signals are replaced with one singlet (6-H) and two doublets (3-H and 4-H) in the complexes [PdX(pma)] (X = Cl, Br) with reduction in intensity by one proton. This indicates that one of the ring protons is lost (Structure I). In accordance with this fact, the infrared spectra show bands at 818 and 877 cm^{-1} characteristic of a 1,2,4-trisubstituted benzene ring [9]. Lower frequency shift of the amide I band (mainly ν(C=O)) and higher frequency shift of the amide II band (mainly ν(C–N) and δ(N–H)) of the amide group [10] of [PdCl(pma)] show coordination of the amide-oxygen atom (Structure I), while for [PdBr(pma)] the assignment of the amide I band is not unambiguous (Table II) and coordination of the group is difficult to determine. Strong coupling between the amide bands and ν(C=N) of the imino group (–$C(CH_3)$=N–) may be operative and ν(NH) is at an exceptionally high frequency compared with that of the other complexes.

TABLE II. Infrared and PMR Spectra of the Ligands and the Complexes.

Compound	Infrared (cm^{-1})[a]					PMR(δ, ppm)[b]		
	ν(NH)	Amide I	Amide II	π(NH)	ν(PdX)	CH_3	NH	Ring Protons[c]
Hpma	3195	1675	1460	740		2.23s(2Me)[d] 2.37s	10.43s	7.76d, 7.27d (8.2)
[PdCl(pma)]	3265	1604	1501	503	325	2.30s(2Me) 2.05s	10.8br	7.35d, 7.00d (7.7), 7.58s
[PdBr(pma)]	3440	1590[e], 1658	1534	565br	228	2.28s(2Me) 2.06s	11.0br	7.28d, 6.94d (7.5), 7.65s
[PdCl(pma)py]	3265	1689 1706	1478	570	238	2.29s 2.18s(2Me)	9.7br	7.22d, 6.93d (8.0), 6.07s[f]
Hafa	3190	1661	–[g]	736		2.17s(2Me)	10.14s	4.66t, 4.39t (1.9), 4.21s
[PdCl(afa)]	3190	1661	1478	739	260 222	1.99s 2.17s	10.1s	5.15d, 4.77d, 4.56t (2.4), 4.45s
[PdBr(afa)]	3240	1566	1515	566	203	1.99s 2.17s	10.1s	5.16d, 4.74d, 4.51t (2.4), 4.44s
[PdCl(afa)py]	3200	1667	1480	723	246	2.17s(2Me)	9.1br	4.36s, 4.32t (2.4) 4.49dd, 3.98dd (2.4, 0.8)
Hata	3165	1666	–[g]	708		2.32s 2.22s	10.47s	7.17dd (5.0, 3.8) 7.4–7.7 m
[PdCl(ata)]	3240	1585	1501	519	363[h] 287	2.30s 2.05s	10.5br	7.56d, 7.83d (4.8)
[PdBr(ata)]	3238	1581	1498	495	217	2.28s 2.08s	10.5br	7.50d, 7.79d (4.8)
[PdCl(ata)py]	3240	1664 1698	1462	578	242	2.32s 2.18s	9.19s	6.33d, 7.40d (4.8)
[PdBr(ata)py]	3210	1664	1459	593		2.32s 2.19s	9.14s	6.35d, 7.37d (4.8)
[PdCl(ata)PBu_3]	3300	1696	1461	588	293	2.34s 2.17s	9.43s	7.46dd (4.0, 1.1) 6.95dd (4.0, 0.9)

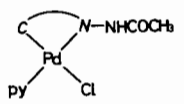
[a]Nujol mulls and KBr discs. [b]Dmso-d_6 solutions with DSS as an internal standard except for the py and PBu_3 complexes for which $CDCl_3$ and TMS are used. [c]Coupling constants (J) are indicated in parentheses (Hz). [d]Overlapped signals. [e]Cannot assign unambiguously. [f]Signals due to py and PBu_3 are not included in this Table. [g]Cannot be assigned. [h]May be coupled bands (see ref. 7).

The PMR spectrum of Hafa shows two triplets due to the monosubstituted cyclopentadienyl ring and the spectra of [PdX(afa)] show two doublets (3-H and 5-H) and one triplet (4-H). Strong singlets with an intensity 5 H are observed for both Hafa and [PdX(afa)] to reveal the presence of an unsubstituted cyclopentadienyl ring. The presence of an *ortho*-disubstituted cyclopentadienyl ring is inferred [11]. No shift of the amide I band of [PdCl(afa)] suggests non-coordination of the amide group in the solid state (Structure II) but the band of [PdBr(afa)] appears at an appreciably lower frequency suggesting coordination of the amide-oxygen atom (Table II). The structure of [PdBr(afa)] corresponds to Structure I.

The spectroscopic data of Hata and [PdX(ata)] (X = Cl, Br) (Structure III) are discussed in a preliminary communication of this research [7] and the PMR spectral patterns of thiophene ring protons are depicted there.

The complexes [PdXL] react easily with pyridine (py) to give the adducts [PdXL(py)]. The adducts show infrared and PMR spectra similar to those of the original complexes excepting the signals and bands discussed below. The modes of coordination of the hydrazones do not, therefore, change seriously.

The singlet (6-H) of phenyl ring protons of [PdCl(pma)py] is strongly shielded (Table II) compared with that of [PdCl(pma)]. The shielding can be explained in terms of Structure IV, in which the



IV

pyridine ring is nearly perpendicular to the coordination plane because of steric hindrance between 6-H of the phenyl ring and 2-H and 6-H of the pyridine ring. Thus 6-H of the phenyl ring lies nearly above the pyridine ring and is shielded by the aromatic ring current. Appearance of ν(PdCl) at a low frequency is consistent with Structure IV where Cl atom is situated *trans* to a carbon donor with high *trans* influence. The amide I band is observed at a high frequency and the amide II band at a low frequency (Table II) to reveal non-coordination of the group. The ferrocene analogue [PdCl(afa)py] shows a high field doublet (5-H) and Structure IV is also proposed, for 5-H of a substituted cyclopentadienyl ring lies nearly above the pyridine ring in the structure. Non-coordination of the amide group is clearly suggested by the amide bands.

One (4-H) of the two doublets of thiophene ring protons is strongly shielded in the complexes [PdX(ata)py] like in the above mentioned complexes [PdClL(py)] (L = pma and afa), while in the complex [PdCl(ata)PBu_3] without any aromatic ring current the two doublets (4-H and 5-H) appear in a field near that in which the signals are observed for [PdCl(ata)]. Both doublets of [PdCl(ata)PBu_3] show additional small splitting (Table II) probably due to long range coupling, J(P–H). The infrared spectra of the complexes show ν(PdCl) at low frequencies and the amide bands suggest non-coordination of the group. Structure IV is, therefore, confirmed for [PdX(ata)py] and [PdCl(ata)PBu_3]. The splitting of the amide I band of [PdCl(ata)py] (and also [PdCl(pma)py]) may result from coupling of the amide I band with ν(C=N), or from the presence of different conformers of the amide group (*cis*- and *trans*-amide group) [12]. The considerable difference in frequencies of ν(PdCl) between the two chloro complexes [PdCl(ata)py] and [PdCl(ata)PBu_3] may be due to coupling with other modes of vibration and/or different hydrogen bonding of Cl with neighboring groups. ν(PdBr) is not observed down to 200 cm^{-1} (the limit of our spectrometer) since Br is coordinated *trans* to a carbon donor with high *trans* influence (Structure IV).

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