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SYNTHESIS OF SEVERAL CYCLOPALLADATED BIACETYLMONOXIME ARYLHYDRAZONES

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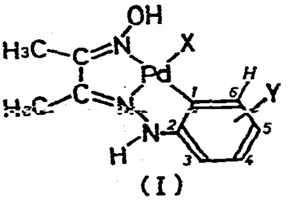
Summary

Palladium(II) complexes of biacetylmonoxime arylhydrazones (HL, aryl = phenyl, *o*-, *m*-, and *p*-tolyl, *p*-chloro- and *p*-nitrophenyl) and biacetylmonoxime *N*'-methyl-phenylhydrazone (HL') have been prepared and characterized. The hydrazoximes, HL and HL', are coordinated through oxime- and hydrazone-nitrogen atoms as a bidentate ligand in the complexes [PdX$_2$(HL or HL')] (X = halogen atom) formed under neutral conditions. Under basic conditions the deprotonated complexes [PdX(L or L')] are obtained. Deprotonation occurs at the oxime group of HL' and the ligand remains coordinated through oxime- and hydrazone-nitrogen atoms. The other hydrazoximes (HL) are cyclopalladated at the *ortho* position of the benzene rings and act as an N—N—C terdentate ligand in the deprotonated complexes [PdXL].

Introduction

Various Schiff bases and hydrazones of biacetylmonoxime are frequently used as ligands and their transition metal complexes have been investigated in some detail [1]. So far no evidence has been reported for cyclometallation reactions of these ligands. We have found that arylhydrazones of biacetylmonoxime are cyclometallated in the palladium(II) complexes. The complexes have a fused organometallic chelate ring (I), which seems to be rare since a large number of



(I)

TABLE 1

ABBREVIATIONS USED FOR HYDRAZOXIMES

Hydrazoxime	Abbreviation
Biacetylmonoxime phenylhydrazone	Hphh
o-tolylhydrazone	Hoth
m-tolylhydrazone	Hmth
p-tolylhydrazone	Hpth
p-chlorophenylhydrazone	Hpch
p-nitrophenylhydrazone	Hpnh
N'-methyl-phenylhydrazone	Hmph

the known cyclometallated complexes do not have fused chelate rings [2]. The reaction may be useful in organic synthesis. A preliminary report of this research has appeared [3].

Results and discussion

The hydrazoximes (HL) shown in Table 1 react with lithium tetrachloropalladate in methanol in the presence of sodium acetate to give the complexes [PdClL] (Table 2), in which the hydrazoximes are deprotonated. The complexes of the type [$PdCl_2$(HL)] are prepared without addition of sodium acetate and those of Hpth and Hmph are characterized. The proposed reaction scheme is shown in Scheme 1.

The PMR spectra of the free hydrazoximes measured in dmso-d_6 show low field resonances (δ = 8—12 ppm from DSS = sodium 2,2-dimethyl-2-silapentane-

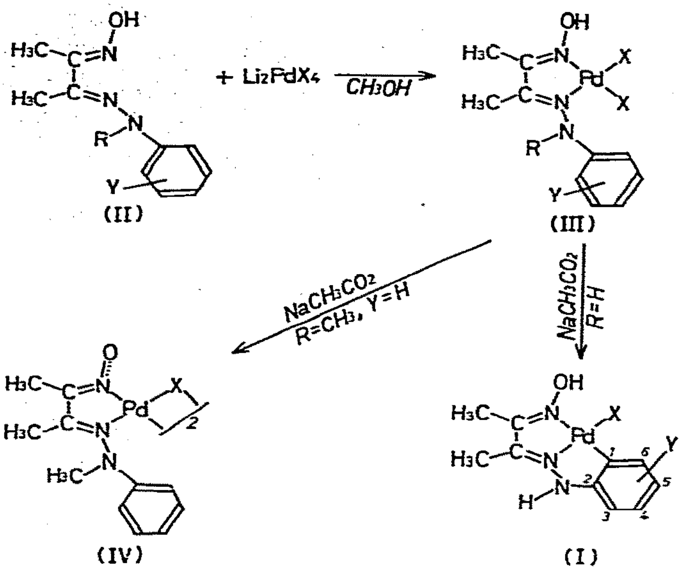
TABLE 2

MELTING POINTS, YIELDS, AND ANALYTICAL RESULTS FOR THE COMPLEXES

Complex	M.p. [a] (°C)	Yield (%)	Analysis: found (calcd.) (%)		
			C	H	N
$PdCl_2$(Hpth)	185	71	34.29(34.54)	3.82(3.95)	11.01(10.98)
$PdBr_2$(Hpth)	195	79	28.22(28.02)	3.06(3.21)	8.97(8.91)
$PdCl_2$(Hmph)	175	57	34.05(34.54)	3.91(3.95)	10.69(10.98)
PdCl(phh)	220	84	36.15(36.17)	3.52(3.63)	12.48(12.65)
PdBr(phh)	200	68	31.75(31.90)	3.14(3.21)	11.02(11.16)
PdCl(oth)	215	87	38.44(38.17)	4.11(4.08)	12.17(12.14)
PdCl(mth)	220	67	38.04(38.17)	4.12(4.08)	12.09(12.14)
PdCl(pth)	225	81	38.54(38.17)	4.12(4.08)	12.21(12.14)
PdBr(pth)	200	82	34.01(33.83)	3.67(3.61)	10.64(10.76)
PdI(pth)	190	80	30.12(30.20)	3.13(3.20)	9.31(9.60)
PdCl(pch)	220	90	32.96(32.77)	2.87(3.03)	11.48(11.46)
PdI(pch)	200	75	26.15(26.23)	2.49(2.42)	8.99(9.18)
PdCl(pnh)	250	23	31.75(31.85)	2.77(2.94)	14.47(14.85)
PdCl(mph)	210	76	38.12(38.17)	4.20(4.08)	11.96(12.14)
PdBr(mph)	185	73	34.03(33.83)	3.59(3.61)	10.77(10.76)
PdCl(mph)(PPh_3)	215	73	57.31(57.25)	5.26(4.80)	6.77(6.91)

[a] Decomposition occurred without melting.

SCHEME 1. Proposed reaction scheme.



sulfonate) due to oxime- and hydrazone-protons, which disappear upon addition of D_2O. These signals remain in the PMR spectra of the complexes, except for [PdX(mph)] (X = Cl, Br), which have no signal in this region (Table 3) and no absorption assignable to ν(O—H) of an oxime group in the infrared spectra. The IR spectrum of the non-deprotonated complex of the same ligand [$PdCl_2$(Hmph)], however, shows a strong band at 3165 cm^{-1} for the oxime OH group and the

TABLE 3

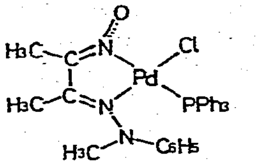
INFRARED SPECTRA [a] AND PMR SPECTRA [b] OF THE COMPLEXES

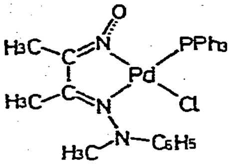
Complex	Infrared (cm^{-1})		PMR spectra, δ (ppm from DSS)			
	ν(Pd—X)	ν(N—O)	OH	NH	CH_3	Aromatic-H
$PdCl_2$(Hpth)	356, 301	1081	ca. 5.3 [c]		2.08(2Me), 2.25	7.10
$PdBr_2$(Hpth)	240, 205	1081	ca. 5.1 [c]		2.08(2Me), 2.25	7.10
$PdCl_2$(Hmph)	329, 281	1078	ca. 5.0 [c]		2.16, 2.33, 3.32	6.5—7.6
PdCl(phh)	304	1060	11.24(br)	10.41	2.06, 2.16	6.3—7.3
PdBr(phh)	209	1057	11.0(br)	10.56	2.06, 2.11	6.3—7.4
PdCl(oth)	310	1060	11.47(br)	9.41	2.10, 2.18, 2.23	6.3—7.2
PdCl(mth)	332	1060	11.40(br)	10.42	2.04, 2.12, 2.17	6.97d, 6.37m
PdCl(pth)	341	1058	11.18(br)	10.33	2.05, 2.12(2Me)	6.91s, 6.67d, 6.38d
PdBr(pth)	200	1058	10.87(br)	10.42	2.06, 2.12(2Me)	7.11s, 6.69d, 6.36d
PdI(pth)		1067	10.32(br)	10.48	2.03, 2.09(2Me)	7.49s, 6.68d, 6.38d
PdCl(pch)	300	1062	11.43(br)	10.65	2.05, 2.14	7.06s, 6.95d, 6.48d
PdI(pch)		1055	10.7(br)	10.78	2.05, 2.13	7.65s, 6.93d, 6.51d
PdCl(pnh)	322	1058	11.40(br)		2.09, 2.23	7.92s, 7.86d, 6.64d
PdCl(mph)	329, 288	1226			2.00, 2.23, 3.30	6.5—7.6
PdBr(mph)	210	1223			1.83, 2.24, 3.27	6.6—7.6

[a] Nujol mull. [b] In dmso-d_6. [c] Exchanging of protons between H_2O contaminated in dmso-d_6 and OH and NH seems to occur. br = broad, m = multiplet, s = singlet, d = doublet.

band characteristic of an N-coordinated oxime group is found at 1078 cm^{-1} (Table 3) [1,4]. The two strong bands at 329 and 281 cm^{-1} are assigned to ν(Pd—Cl) and structure III is reasonable for $[PdCl_2(Hmph)]$. The deprotonated complexes [PdX(mph)] show new strong bands at 1226 (Cl) and 1223 (Br) cm^{-1}, the bands being due to a deprotonated, N-coordinated oxime group [5]. The mode of coordination shown in structure IV is proposed. The coordination mode is further supported by the fact that the PMR spectra show that there are five phenyl protons. The two bands at 329 and 288 cm^{-1} in the IR spectrum of [PdCl(mph)], which are absent in that of the bromo analogue, are assigned to ν(Pd—Cl), and a halogen bridge is tentatively proposed *.

Triphenylphosphine (PPh_3) reacts smoothly with [PdCl(mph)] to give the adduct $[PdCl(mph)(PPh_3)]$, which may suggest the presence of a bridging group in [PdCl(mph)] [8]. The adduct has a strong band at 358 cm^{-1} due to ν(Pd—Cl) in its infrared spectrum. In the PMR spectrum measured in $CDCl_3$, the aromatic ring protons appear as a complex pattern in the region 6.7—8.0 ppm. The signal of one of the CCH_3's is at 1.78 ppm, while that of the other CCH_3 is split into two; one at 2.18 and the other at 2.26 ppm with relative intensity 5 : 12. A singlet at 3.37 and a doublet at 3.51 ppm (J = ca. 2 Hz) with relative intensity 5 : 12 are due to NCH_3. The presence of two isomers, Va and Vb, is suggested. If the small coupling arises from ^5J(P—H) [9], the more abundant isomer may be Vb. Separation of the isomers was not attempted.


(Va)


(Vb)

The infrared spectra of $[PdX_2(Hpth)]$ (X = Cl, Br) show ν(O—H) and ν(N—H) of oxime and hydrazone groups in the region 3250—3300 cm^{-1} and also ν(Pd—X) as shown in Table 3. The band at 1081 cm^{-1} is assigned to the oxime group. The PMR spectra reveal that the number of aromatic ring protons is not reduced as compared with those of the free ligand. Structure III is proposed (Scheme 1).

It is very interesting that the PMR spectra of the deprotonated complexes [PdXL] (L = other than mph) show two low field resonances, which disappear upon addition of D_2O. They are assigned to oxime- and hydrazone-protons. In addition the infrared spectra show ν(O—H) and ν(N—H) in the region 3250—3450 cm^{-1}, and ν(N—O) of oxime groups at ca. 1060 cm^{-1} (Table 3). These facts imply that the oxime and hydrazone groups remain protonated in the deprotonated complexes [PdXL] as in the protonated complexes $[PdX_2(HL)]$.

The PMR spectra of the deprotonated complexes (Table 3) show that one aromatic ring proton is lost and the other protons are more shielded than those in the free ligands. The *para*-substituted derivatives have, in general, a singlet and

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* Dimeric complexes with bridging oxime groups (N- and O-coordination) are known [6,7] and a similar oxime bridge cannot be excluded.

two doublets in the region of aromatic ring protons (small couplings (<2 Hz) are ignored). The singlet is assigned to 6-H (proton on carbon *ortho* to a Pd—C bond) and the two doublets to 3-H and 4-H. Characteristic infrared spectral bands of 1,2,4-tri-substituted benzene rings [10] are found at 887 (pth), 893 (pch), and 902 (pnh) cm^{-1}. Structure I is, therefore, confirmed.

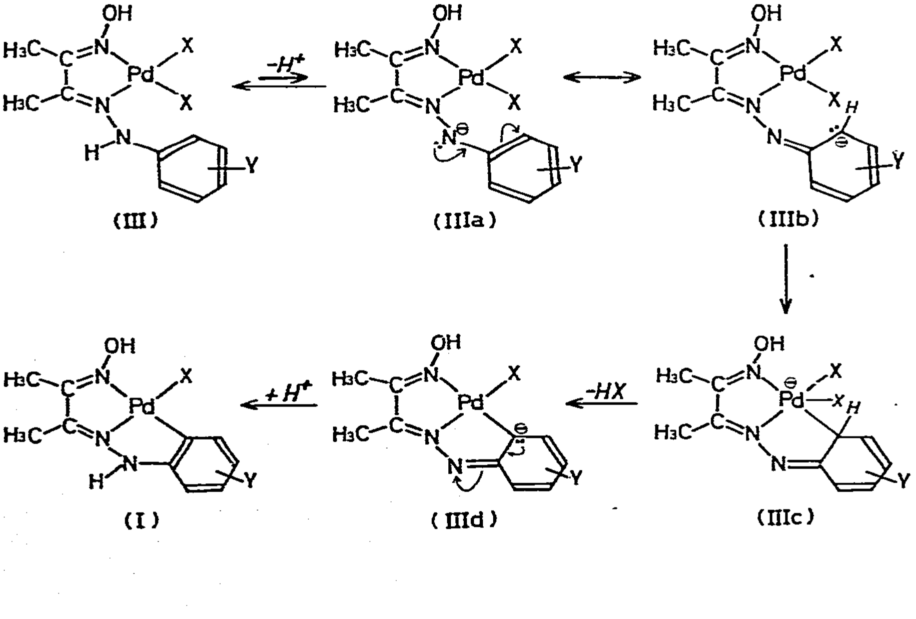
The low field resonances assigned to oxime protons show halogen-dependence (Table 3) and the protons are shielded in the order $Cl < Br < I$. The reversed order of shielding is found for 6-H of the benzene rings. The oxime protons and the 6-H are in the proximity of the coordinated halogen atoms. Hydrogen bonding is possible for the oxime protons. The infrared spectrum of [PdX(pth)] shows two bands at 3320(sh), 3275 (Cl), 3390, 3295 (Br), and 3418, 3280 (I) cm^{-1}, the more halogen dependent one at a higher frequency being assigned to oxime groups and hydrogen bonding between oxime groups and halogen atoms is presumed.

Hydrogen bonding of the 6-H is, however, impossible and the order of deshielding is the same as that of increasing van der Waals radii of halogens. Increasing interaction in the space between 6-H and X with the increasing radii may be the origin of the deshielding which has been reported for some sterically crowded organic molecules [11]. The same trend of the chemical shifts of protons with progressive approach to halogen atoms has been reported for several square-planar and octahedral complexes [12].

The hydrazone-protons of the cyclopalladated, *p*-substituted hydrazoximes are deshielded in the order of the substituents: $CH_3 < H < Cl < NO_2$ (Table 3). This is the order of increasing electron withdrawal and the electron density of the hydrazone groups should be decreased in this order. Only the proton of [PdCl(oth)] resonates at an exceptionally high field and this may be from strong shielding by the *ortho* methyl group.

The presence of a hydrazone-proton is of great importance in cyclopalladation

SCHEME 2. Possible mechanism activating an *ortho* C—H bond.



reactions of hydrazoximes, since biacetylmonoxime N'-methyl-phenylhydrazone (Hmph) cannot be cyclopalladated and the oxime group is deprotonated to form complexes with structure IV. The role of the hydrazone-proton is probably to increase the electron density of the *ortho*-carbon atom which is subjected to electrophilic attack by a palladium atom [2]. One possible mechanism of increasing the electron density under basic conditions is deprotonation of the hydrazone group as shown in Scheme 2. Activation of this mechanism may make it possible to cyclopalladate a nitro substituted benzene ring which is otherwise fairly unreactive.

Experimental

Preparation of [PdX$_2$(HL)]

To a mixture of 1 mmol of palladium chloride and 2.5 mmol of lithium chloride (or bromide) in 40 ml of methanol was added 1 mmol of biacetylmonoxime arylhydrazone. The mixture was stirred for one day at room temperature and a yellow-brown precipitate was collected, washed with methanol, and then dried in air. The yield is shown in Table 2.

Preparation of [PdXL]

To the mixture prepared as above by mixing palladium chloride, lithium chloride, and the hydrazoxime in methanol was added 1 mmol of sodium acetate. The resulting mixture was dark brown but gradually turned orange. It was stirred at room temperature until no further color change was observed (usually for several days). The orange product was treated as above. The yield is shown in Table 2. The metathesis reaction of [PdClL] with lithium bromide or iodide in dimethyl sulfoxide gave the corresponding bromide or iodide, respectively. The products could be recrystallized from acetone.

Measurements

All the measurements were carried out by the methods previously reported [12].

Acknowledgement

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