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RESEARCH ARTICLE

Synthesis, Characterization of Substituted Piperdin-4-ones with Dichloro(cyclooctadiene)palladium(II)

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Abstract: The complexes were synthesized using substituted 2,6-diphenyl piperdin-4-ones (ligands) and dichloro(cyclooctadiene) palladium(II) (precursor) in dichloromethane (solvent). In the present study we report the synthesis and characterized by infrared and NMR studies on substituted 2,6-diphenylpiperdin-4-ones and their palladium(II)complex.

Keywords: Synthesis, 2,6-Diphenyl piperdin-4-ones, Precursor, Dichloro(cyclooctadiene) palladium(II)

Introduction

4-Piperidone play an important role which embraces the organometallic field in different ascepts[1-5]. 2,6–Diphenyl–4-piperidone and their metal complexes have a variety of applications in numerous scientific areas. By exhibiting a wide range of pharmacological activities[6-12] a series of 2,6–diphenyl–4-piperidone were synthesized by different dialkyl ketone, aromatic aldehyde and ammonium acetate by Mannich condensation reaction[13]. The formation of an interesting array of new compounds we reported the synthesis of substituted 2, 6–diphenyl–4-piperidone with palladium metal by the formation of an interesting array of new compounds. These palladium (II) complexes have gained more significant applications.

Experimental

The reagent grade chemicals and reagents were purchased from AR grade and purified by either distillation or recrystallization before use. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) with silica gel plates.

Physical measurements

Melting points of the synthesized compounds were taken in open glass capillaries using a Barnstead 9001 electro thermal melting point apparatus and are uncorrected. Infrared (IR) spectra (ν, cm^{-1}) were recorded on a Shimadzu FT/IR-330E, Fourier Transform Infrared Spectrometer using KBr discs. Nuclear Magnetic spectroscopic (NMR) measurements ^{1}H NMR and ^{13}C NMR spectra were noted by Jeol GSX 4OONB NMR spectrometer operating at 500.13 MHz and 125.76 MHz with $DMSOd_6$ as solvent and tetramethylsilane (TMS) as an internal standard.

Synthesis of substituted 2, 6-diaryl piperidin-4-ones (L_1-L_9)

The general procedure for the preparation of substituted piperdin-4-ones is reported by literature method[13]. The ligands (L_1-L_9) were prepared by refluxing a mixture of substituted aldehydes, dry ammonium acetate and dialkyl ketones (2:1:1) in the presence of ethanol (30 mL). This reaction mixture was allowed to stand overnight at room temperature followed by adding concentrated hydrochloric acid (30 mL).Then the precipitated hydrochloride was collected and washed with ethanol and ether mixture (1:5) and it was transferred to one litre beaker. The hydrochloride was suspended in acetone and basified with a strong ammonia solution. On dilution with excess of water the free base was separated out. The product was filtered, washed with water and dried. Crystallization of the product from ethanol results in substituting piperidin-4-ones. The structure of substituted piperidin-4-ones ligands as shown in Figure1.

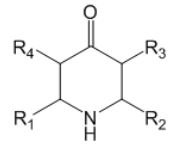

Figure 1. Structure of substituted piperidin-4-ones ligands

Ligand	Ligand name	R_1	R_2	R_3	R_4
L_2	3-Methyl-2,6-diphenylpiperidin-4-one	C_6H_5	C_6H_5	CH_3	H
L_2	3,5-Dimethyl-2,6-diphenylpiperin-4-one	C_6H_5	C_6H_5	CH_3	CH_3
L_3	3-Ethyl-2,6-diphenylpieridine-4-one	C_6H_5	C_6H_5	C_2H_5	H
L_4	3-Methyl-2,6-ditolylpiperidin-4-one	$C_6H_4CH_3$	$C_6H_4CH_3$	CH_3	H
L_5	3,5-Dimethyl-2,6- ditolylpiperidin-4-one	$C_6H_4CH_3$	$C_6H_4CH_3$	CH_3	CH_3
L_6	3-Ethyl-2,6- ditolylpiperidin-4-one	$C_6H_4CH_3$	$C_6H_4CH_3$	C_2H_5	H
L_7	3-Methyl-2,6-dianisylpiperidin-4-one	$C_6H_4OCH_3$	$C_6H_4OCH_3$	CH_3	H
L_8	3,5-Dimethyl-2,6- dianisylpiperidin-4-one	$C_6H_4OCH_3$	$C_6H_4OCH_3$	CH_3	CH_3
L_9	3-Ethyl-2,6- dianisylpiperidin-4-one	$C_6H_4OCH_3$	$C_6H_4OCH_3$	C_2H_5	H

Preparation of palladium(II) ion complexes(C_1-C_9)

The dichloro(cyclooctadiene)palladium (II) is used as a precursor. The dichloro (cyclooctadiene) palladium(II) with 2, 6-diaryl piperidin-4-ones ligands (L_1-L_9) were prepared by the following procedure: A mixture of dichloro(cyclooctadiene) palladium(II) (0.5 m mol) and substituted piperidin-4-ones (L_1-L_9) (0.5 m mol in dichloromethane (50 mL) was refluxed for 5 h. The solvent was then distilled off under reduced pressure. The residue was repeatedly washed with hot ethanol, acetone and ether remove the unreacted piperidin-4-one and then dried through in *vacuo* phosphorus (V) oxide.

Results and Discussion

The general schematic representation describing the routes of synthesis was furnished in Figure 2. By the condensation of substituted aldehyde, ammonium acetate and dialkyl ketones in the ratio of 2:1:1 for obtaining substituted 2, 6-diarylpiperdin-4-ones. All the synthesized substituted 2, 6-diarylpiperdin-4-ones are soluble in solvents such as ethanol, methanol, dimethylsulphoxide, dichloromethane and ether but insoluble in water. They are stable in air under dry conditions. Palladium(II) complexes are dull yellowish in colour. The structure of the synthesized substituted 2, 6-diarylpiperdin-4-ones is established on the basis of IR and NMR (^{1}H and ^{13}C) data obtained as given in Table 1,2 and 3.

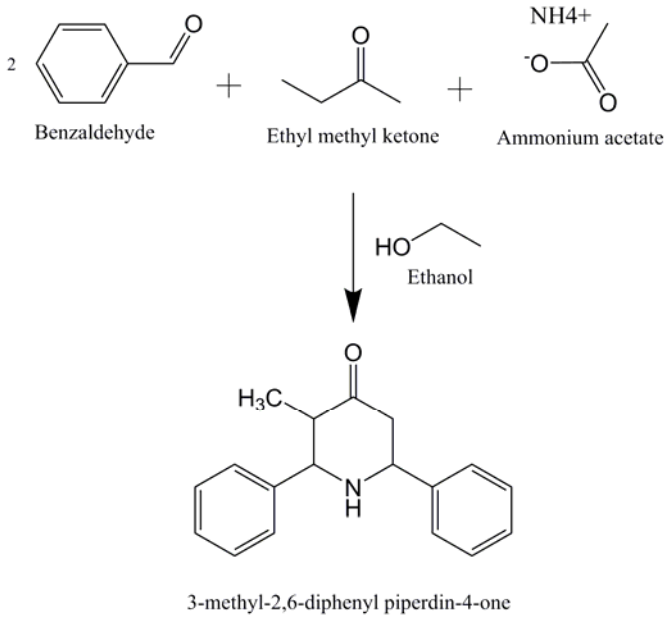

Figure 2. Synthesis of 3-methyl-2,6-diphenylpiperidin-4-one

IR Spectra for ligands and complexes

The infrared spectra for ligands (L_1-L_9), shows an absorption band lies around 1700 cm^{-1} and 3300 cm^{-1} C=O groups and NH groups. In Palladium complexes (C_1-C_9), it is shifted corresponding of the ligands are recorded in Table 1.

Table 1. IR spectral data for ligands and complexes

Complex	IR							
	ν(C=O)[a]	ν(C=O)[b]	ν(N-H)	ν(O-H)	ν(HOH)	ν(Ar-H)	ν(M-N)	ν(M-O)
C_1	1710	1716	2928	3200-3700	1633	802	698	435
C_2	1712	1716	2924	3200-3700	1624	868	551	513
C_3	1713	1716	2924	3200-3700	1625	867	547	460
C_4	1697	1716	2928	3200-3700	1631	810	516	451
C_5	1712	1716	3207	3200-3700	1620	817	516	455
C_6	1720	1722	2926	3200-3700	1618	812	514	422
C_7	1705	1716	2928	3200-3700	1621	829	536	424
C_8	1701	1718	3209	3200-3700	1612	804	540	401
C_9	1707	1714	3089	3200-3700	1612	831	538	418

$\nu(C=O)^a$-for ligands; $\nu(C=O)^b$- for complexes

^{1}H-NMR spectra

The nine complexes (C_1.C_9) were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectral data shows a singlet at δ2.5 ppm to NH protons are given in Table 2.

Table 2. ^{1}H NMR spectral data for complexes

NMR	Complex								
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
H(2)(s,1H)	3.327	3.332	3.344	3.344	3.322	3.502	3.359	3.363	3.336
H(3) and H(5)(m,3H)	2.148	2.508	2.509	3.790	3.402	2.740	3.781	3.608	3.796
H(6) (s,1H)	3.584	3.514	4.728	4.145	4.412	3.344	5.511	5.489	5.502
C(3)-R(d,3H)	0.668	0.664	0.717	0.770	0.629	0.731	0.642	0.624	0.720
NH(s,1H)	2.501	2.306	2.509	2.506	2.502	2.505	2.505	2.504	2.504
Aromatic protons	7.735 - 7.865	7.394 - 7.540	7.426 - 7.516	6.437 - 7.611	7.268 - 9.994	7.426 - 10.544	7.125 - 7.750	6.910 - 7.375	7.452 - 10.790

^{13}C NMR spectra

^{13}C NMR spectrashows a peak δ204 ppm for C=O group in C_4 carbon by shifting the position on complexion with precursor Table 3.

Table 3. ^{13}C NMR spectral data for complexes

NMR	Complex								
	C_1	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**	**C_9**
C(2)	70.417	70.281	68.172	60.321	70.185	63.416	67.553	67.849	61.953
C(3)	64.126	64.561	64.068	53.901	64.649	59.560	60.508	55.460	55.563
C(4)	204.320	209.018	206.940	208.270	209.159	203.821	209.673	211.590	210.123
C(5)	56.140	48.328	59.432	49.449	48.932	45.266	55.769	51.421	51.466
C(6)	46.266	40.264	40.187	40.190	40.280	40.265	40.184	40.196	40.276
C(3)-R	11.180	11.167	11.134	10.806	11.180	11.114	11.837	11.119	12.076
Aromatic carbons	127.430 - 128.880	128.878 - 138.322	128.722 - 139.218	106.065 - 155.696	127.248 - 139.151	128.828 - 135.722	110.052 - 128.877	129.151 - 135.080	128.256 - 130.032

Conclusion

From the above results and discussion for a series of substituted piperdin-4-one ligands (L_1-L_9) and their complexes (C_1-C_9) were synthesized and characterized successfully.

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