Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

THE SYNTHESIS AND INFRARED SPECTRA OF DI-μ-CHLOROBIS-[*o*-(*N*-PHENYLFORMIMIDOYL)PHENYL]DIPALLADIUM(II) AND RELATED COMPLEXES

STEPHEN P. MOLNAR AND MILTON ORCHIN
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221 (U.S.A.)

(Received September 16th, 1968)

INTRODUCTION

Azobenzene complexes of nickel(II)[1], palladium(II)[2], platinum(II)[2] and cobalt(III)[3] have been reported and although there is little question about the major features of structure of these complexes, the question of which azo nitrogen atom is coordinately bonded to the metal has not been unequivocally demonstrated. In order to help answer this question and in order to define further the features of structure which are responsible for the remarkable stability of these complexes, we have prepared a series of analogous Pd^{II} complexes of structure (I), using the isoelectronic benzylideneaniline* as the organic moiety. The IR spectra of these complexes were expected to be useful for structure determination.

EXPERIMENTAL

Synthesis of benzylideneanilines

These compounds were synthesized by refluxing equimolar amounts of appropriate anilines and appropriate aldehydes or ketones in methanol for 1 h. The resulting benzylideneanilines were recrystallized from aqueous methanol or distilled under reduced pressure. A known modified method[4] was employed to prepare sterically hindered benzylideneanilines.

Synthesis of (benzylideneaniline)palladium(II) chloride complexes

In a typical experiment 1.04 mmoles of bis(benzonitrile)palladium(II) dichloride was dissolved in 100 ml of methanol with slight warming. A solution of 5 mmoles of benzylideneaniline in 100 ml of methanol was added and the reaction mixture was heated to reflux. The color of the reaction mixture changed from dark red to yellow almost immediately on mixing and the solution became cloudy several minutes after reaching the reflux temperature. After refluxing for 3 h the reaction mixture was cooled to room temperature, filtered, and the complex washed with methanol. The complexes

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* Instead of the systematic but formidable name of these complexes which appears in the title we abbreviate the parent compound (I) as $[BzaPdCl_2]_2$.

TABLE 1

BIS[(BENZYLIDENEANILINE)PALLADIUM(II) CHLORIDE] COMPLEXES (I)

Substituent			Ligand (mmoles)[a]	Product			
				Yield (%)[b]	M.p. (°C)	% Pd[c]	
						Calcd.	Found
4-	*4'-*						
H	H		5.03	96.0	286–8(d)	32.9	32.5
OCH_3	H		5.02	94.3	240–5(d)	30.3	30.0
H	OCH_3		5.00	91.5	243–5(d)	30.3	30.2
OCH_3	OCH_3		5.00	97.4	241–3(d)	27.8	28.0
CH_3	H		4.76	83.4	277–85(d)	31.6	31.6
H	CH_3		5.18	61.9	235–40(d)	31.6	32.0
CH_3	CH_3		5.03	51.5	240–5(d)	30.4	28.0
Cl	H		5.02	77.1	241–3(d)	29.9	30.0
H	Cl		5.00	33.0	241–3(d)	29.9	29.8
Cl	Cl		5.00	82.0	275–80(d)	25.3	25.0
NO_2	H		5.00	79.0	250–3(d)	29.0	28.5
H	NO_2		5.05	97.2	285–8(d)	29.0	29.2
NO_2	NO_2		5.00	95.0	250–5(d)	25.8	25.5
3-	*3'-*						
H	CH_3		5.01	29.5	255–60(d)	31.6	29.5
H	Cl		5.00	89.9	280–5(d)	29.9	30.1
NO_2	H		5.00	95.0	262–5(d)	29.0	28.7
H	NO_2		5.00	87.2	330–5(d)	29.0	28.5
NO_2	NO_2		5.02	85.5	290–5(d)	25.8	26.0
α-	*2'-*	*6'-*					
CH_3	H	H	4.96	84.5	285–90(d)	31.7	31.5
H	CH_3	CH_3	5.22	91.5	248–55(d)	29.1	29.4
CH_3	CH_3	CH_3	5.12	89.0	290–5(d)	26.7	26.5
C_6H_5	H	H	5.02	75.0	300–5(d)	30.4	29.5
C_6H_5	CH_3	CH_3	5.00	80.0	345–8(d)	25.0	24.9
2-	*4-*	*6-*					
CH_3	CH_3	CH_3	5.00	85.0	260–5(d)	26.6	26.4

[a] One mmole of $PdCl_2(PhCN)_2$ used in all experiments. [b] Based on $PdCl_2(PhCN)_2$ as the limiting reagent. [c] Carbon, hydrogen analyses were erratic probably because of retention of carbon by the residue, see ref. 5. In one case, the complex was recovered unchanged after 14 h treatment with hot aqua regia. The complexes were too insoluble for NMR spectra.

which were prepared are listed in Table 1. The melting points are uncorrected and the only analysis performed was the determination of palladium as the bis(dimethylglyoximate).

The IR spectra were determined with a Perkin–Elmer Model 337 Grating Spectrophotometer using Halocarbon oil mulls in the 4000–1333 cm^{-1} region and Nujol in the 1333–400 cm^{-1} region. The reported values are considered to be accurate to only ± 4 cm^{-1}. The results are shown in Tables 2 and 3.

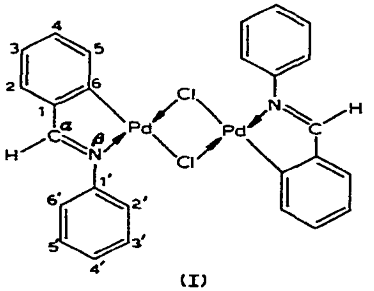
TABLE 2

BENZENE CARBON–HYDROGEN OUT-OF-PLANE BENDING MODES

Substituent		ν(cm^{-1})	
		Ligand	Complex
4-	*4'-*		
H	H	765 s, 690 s	765 s, 760 s, 752 s, 690 s
OCH_3	H	763 s, 720 s, 690 s	775 m, 755 s, 723 w, 690 s
H	OCH_3	762 (sh), 757 m, 752 m, 721 m, 690 s	758 m, 756 m, 735 m
OCH_3	OCH_3	745 w, 730 w	750 w
CH_3	H	773 s, 750 s, 715 s, 693 s	765 s, 760 m, 752 m, 693 s
H	CH_3	760 s, 715 m, 693 s	745 w
CH_3	CH_3	780 m, 720 m, 710 w	745 w
Cl	H	760 s, 712 m, 695 s	760 s, 755 (sh), 748 s, 690 s
H	Cl	758 s, 715 m, 690 s	718 w, 705 w
Cl	Cl	725 m, 700 w	710 w, 700 w
NO_2	H	765 s, 748 s, 695 s	770 s, 759 m, 745 s, 693 s
H	NO_2	752 s, 695 m	760 w, 748 s
NO_2	NO_2	748 s	755 m, 750 m, 745 m
3-	*3'-*		
H	CH_3	785 s, 758 s, 695 s	775 s, 730 s
H	Cl	780 s, 755 s, 693 s	772 s
NO_2	H	767 s, 732 s, 692 s	772 s, 762 s, 690 s
H	NO_2	755 s, 740 s	735 s
NO_2	NO_2	742 s, 735 s	735 s, 720 m

RESULTS AND DISCUSSION

Examination of the IR absorption data of the *free ligands*, Table 2, reveals that only the monosubstituted compounds have a band at approximately 690 cm^{-1}, which is probably an out of plane carbon–hydrogen bending mode[6]. This band is therefore associated with the presence of at least one unsubstituted phenyl ring attached to either atom of the azomethine linkage. Examination of the data for the *complexes* reveals that now the 690 cm^{-1} band is present in the spectra of only those complexes which have an unsubstituted phenyl group attached to the nitrogen atom. These facts argue rather convincingly for the presence of a sigma bond between palladium



(I)

TABLE 3

AZOMETHINE AND AROMATIC RING STRETCHING MODES

Substituent			ν(cm^{-1})			
			Ligand		Complex	
			C=N	C=C	C=N	C=C
4-	*4'-*					
H	H		1640 s	1600 s	1605 s	1590 s
OCH_3	H		1625 s	1605 s	1605 s	1600 s
H	OCH_3		1630 s	1585 m	1610 s	1590 m
OCH_3	OCH_3		1625 s	1605 s	1615 s	1605 s
CH_3	H		1625 m	1585 m	1610 s	1585 s
H	CH_3		1640 s	1590 m	1600 m	1590 s
CH_3	CH_3		1635 s	1580 s	1600 m	1585 s
Cl	H		1630 s	1600 s	1615 m	1600 m
H	Cl		1635 s	1590 m	1605 m	1590 s
Cl	Cl		1635 s	1600 s	1610 m	1600 s
NO_2	H		1640 s	1600 s	1620 m	1600 m
H	NO_2		1635 s	1595 s	1620 m	1595 s
NO_2	NO_2		1635 s	1600 s	1600 m	1600 m
3-	*3'-*					
H	CH_3		1635 s	1600 s	1610 m	1590 s
H	Cl		1635 s	1585 s	1600 s	1585 s
NO_2	H		1625 m	1590 w	1610 m	1590 m
H	NO_2		1635 s	1585 s	1615 m	1585 s
NO_2	NO_2		1640 m	1610 m	1615 m	1600 m
α-	*2'-*	*6'-*				
CH_3	H	H	1640 s	1600 s	1605 s	1590 s
H	CH_3	CH_3	1645 s	1585 m	1605 s	1585 m
CH_3	CH_3	CH_3	1645 s	1585 s	1600 s	1585 s
C_6H_5	H	H	1615 s	1595 s	1600 s	1585 s
C_6H_5	CH_3	CH_3	1620 s	1580 m	1580 s	1575 m
2-	*4-*	*6-*				
CH_3	CH_3	CH_3	1640 s	1580 s	1595 s	1580 s

and a carbon atom on the phenyl ring which is attached to the carbon of the azomethine group.

The IR spectral data of ligands, and of complexes (I) in the 1600–1650 cm^{-1} region are given in Table 3. The spectrum of the free parent benzylideneaniline shows two bands in this region[7]; the band at 1637 cm^{-1} is assigned to the C=N stretching mode while the 1607 cm^{-1} band is assigned to the aromatic ring stretching mode[7]. As Table 3 shows, coordination of benzylideneanilines to palladium always results in a shift of the C=N stretching mode to a lower frequency.

In order to focus on the significance of these data it is instructive to point out that the IR spectrum of benzylideneaniline *N*-oxide, Ph–CH=N(Ph)→O, in which the lone pair on nitrogen is unequivocally involved in σ bonding, has a band at 1600 cm^{-1} which is assigned to the azomethine stretching mode and a band at 1580 cm^{-1} assigned to the aromatic ring stretch. The observed spectral changes in the benzylideneanilines on complexation all parallel the change caused by coordination of the nitrogen lone pair to oxygen in the nitrone. Were complexation through the π-system, a substantially larger decrease in the C=N stretching frequency would be expected. Stretching frequencies of olefins coordinated to Pt or Pd are reduced[8,9] about 150 cm^{-1}. In our series, the C=N stretch is reduced on the average only about 26 cm^{-1}. The position of the aromatic ring stretching frequency shows an average decrease of only 3 cm^{-1} which is about the limit of experimental error. Accordingly, the coordination of benzylideneaniline to palladium is almost certainly through the lone pair and not through the azomethine π-system. There appears to be no simple correlation between the electronic character of the substituent and the change in the azomethine stretching frequency.

In the previous studies of azobenzene complexes with palladium, it was not shown conclusively which nitrogen atom of the azo bridge was bonded to the palladium. Our results demonstrate that the nitrogen atom farthest removed from the palladium phenyl bond is probably involved.

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