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ortho-METALATION REACTIONS OF *N*-PHENYLBENZALDIMINE AND ITS RELATED COMPOUNDS BY PALLADIUM(II) ACETATE

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SUMMARY

Di-μ-acetatobis(2,*N-dihapto-N*-phenylbenzaldimine)dipalladium(II) and related complexes have been prepared by the reaction of *N*-phenylbenzaldimine or related compounds with palladium(II) acetate in boiling acetic acid. Their halogen-bridged analogues have also been prepared by metathetical reactions with sodium chloride or bromide. The present compounds, the structures of which have been confirmed by IR and proton NMR data, are different from those reported by Molnar and Orchin. Reactions of chloro-bridged complexes with triphenylphosphine, pyridine and thallium acetylacetonate have also been carried out.

INTRODUCTION

Recently many reports have appeared on the *ortho*-metalation reactions of aromatic *N*-donor ligands such as azobenzene, *N,N*-dimethylbenzylamine, aromatic oximes, etc., by transition metals[1–5]. Molnar and Orchin[6] reported the synthesis of di-μ-chlorobis(2,*N-dihapto-N*-phenylbenzaldimine)dipalladium(II)* and related complexes by treatment of a series of *N*-phenylbenzaldimines with dichlorobis(benzonitrile)palladium(II), reactions carried out in order to clarify the precise structure of the related azobenzene complex. However, the structure determination was carried out with materials for which satisfactory elemental analyses were not obtained and it was based only on IR spectral data.

In the course of our investigation of olefin arylation catalyzed by palladium(II) salts, we have elucidated that the reaction proceeds via an aryl–palladium σ-bonded intermediate and the best result has been obtained using palladium(II) acetate[7,8], which was reported as a good electrophile for aromatic compounds[9].

In connection with this work, we initially wanted to prepare the above complexes, but several attempted duplications of Molnar and Orchin's procedure resulted in the formation of products having the same IR features as those reported previously except for the presence of coordinated $\nu(NH_2)$ absorptions.

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* The complex was named by Molnar and Orchin as di-μ-chlorobis[*o*-(*N*-phenylformimidoyl)-phenyl]dipalladium(II).

Here we report the preparation of di-μ-acetatobis(2,*N*-*dihapto*-*N*-phenylbenzaldimine)dipalladium(II) and related complexes by the reaction of *N*-phenylbenzaldimine or related compounds with palladium(II) acetate.

RESULTS AND DISCUSSION

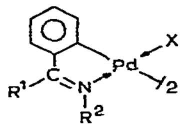
When a methanol solution of dichlorobis(benzonitrile)palladium(II) and *N*-phenylbenzaldimine was refluxed, the yellow crystals which formed, and which had an IR spectrum showing coordinated $\nu(NH_2)$ absorptions at 3280, 3200, 3170(sh) and 3125 cm^{-1}, were found to be a mixture of two complexes. These could be conveniently separated by treatment with dichloromethane. The dichloromethane-insoluble yellow crystals (69% yield) were shown to be dichlorodianilinepalladium(II) by analytical data and by comparing the IR spectrum with that of an authentic sample. Moreover, treatment of the above compound with triphenylphosphine gave aniline and dichlorobis(triphenylphosphine)palladium(II). The dichloromethane-soluble orange crystals (6% yield) were shown to be dichlorobis(*N*-phenylbenzaldimine)palladium(II) by analytical data and by the reaction with triphenylphosphine.

Similarly, *N*-phenylacetophenoneketimine and *N*-(*p*-tolyl)benzaldimine yielded dichlorodianilinepalladium(II), and dichlorodi-*p*-toluidinepalladium(II) and dichlorobis(*N*-(*p*-tolyl)benzaldimine)palladium(II), respectively.

Dichlorodianilinepalladium(II) was probably formed by the methanolysis of *N*-phenylbenzaldimine coordinated to palladium*. Similar metal-assisted cleavage reaction of the azomethine bond was recently reported[4].

Thus, we could not prepare the desired complexes, di-μ-chlorobis(2,*N*-*dihapto*-*N*-phenylbenzaldimine)dipalladium(II) and its analogues, by the procedure reported by Molnar and Orchin. The nature of the complexes reported are not clear at present, but we doubt that they have the structure claimed since their IR spectra are somewhat different from those of our complexes.

In refluxing acetic acid, reaction between *N*-phenylbenzaldimine and palladium(II) acetate afforded di-μ-acetatobis(2,*N*-*dihapto*-*N*-phenylbenzaldimine)dipalladium(II) (Ia) in good yield. A series of related complexes was obtained by the same method from *N*-phenylacetophenoneketimine, *N*-phenylbenzophenoneketimine, *N*-(*p*-tolyl)benzaldimine and *N*-methylbenzaldimine. The corresponding chloro- and bromo-bridged complexes were obtained by the metathetical reaction of acetato-bridged complexes with sodium chloride and bromide in acetone, respectively.



(Ia,b,c) - (Va,b,c)

I: $R^1=H, R^2=C_6H_5$
II: $R^1=CH_3, R^2=C_6H_5$
III: $R^1=C_6H_5, R^2=C_6H_5$
IV: $R^1=H, R^2=p\text{-}CH_3C_6H_4$
V: $R^1=H, R^2=CH_3$
a: $X=CH_3COO$, b: $X=Cl$, c: $X=Br$

The complexes obtained and their IR data are summarized in Tables 1 and 2. The acetato-bridged complexes are soluble in acetone, dichloromethane and

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* After this paper was submitted for publication, the same observation was reported: I. Jardine and F. J. McQuillin, *Tetrahedron Lett.*, (1972) 459.

TABLE 1 IR SPECTRA (cm^{-1})

Compounds	$\nu(C{=}N)$	$\nu(COO^-)$	$\nu(PdCl)$	$\delta(CH)$[a]
Ia		1570, 1410		
Ib	1599		318, 254	761, 745, 713, 694
IIa		1580, 1410		
IIb	1580		299, 256	756, 750, 718, 700
IIIa		1570, 1410		
IIIb	1587[b]		297, 258	753, 723, 702, 692
IVa		1575, 1410		
IVb	1594[b]		320, 257	815, 746, 715
Va		1570, 1410		
Vb	1619		295, 261	755, 750, 714

[a] Benzene carbon–hydrogen out-of-plane bending modes.

[b] Tentative assignment because the band was obscured by absorption due to aromatic ring stretching modes.

TABLE 2 YIELDS, MELTING POINTS AND ANALYSES

Compounds	*Yield* (%)	*M.p.* (°C)[a]	*Analyses, found (calcd.)* (%)			
			C	*H*	*N*	*Mol. wt.*
Ia	96	210–220	52.13	3.71	4.08	677
			(51.52)	(3.75)	(4.12)	(699.38)
Ib	99	281–283	48.59	3.20	4.43	
			(48.47)	(3.14)	(4.35)	
Ic	100	275–276	42.89	2.80	3.68	
			(42.60)	(2.76)	(3.82)	
IIa	99	225–	52.99	4.24	3.85	770
			(53.42)	(4.21)	(3.89)	(719.44)
IIb	93	255–257	50.15	3.68	4.21	
			(50.02)	(3.61)	(4.17)	
IIc	91	267–268	44.45	3.28	3.70	
			(44.18)	(3.18)	(3.68)	
IIIa	87	233–235	60.25	4.11	3.30	872
			(59.80)	(4.07)	(3.32)	(843.58)
IIIb	100	>300	57.74	3.46	3.43	
			(57.31)	(3.55)	(3.52)	
IIIc	94	>300	51.78	3.41	3.13	
			(51.55)	(3.19)	(3.17)	
IVa[b]	89	220–226	49.54	3.94	3.54	748
			(49.27)	(4.02)	(3.48)	(719.44)
IVb	87	293–295	50.32	3.68	4.25	
			(50.02)	(3.61)	(4.17)	
IVc	91	280–281	44.42	3.19	3.94	
			(44.18)	(3.18)	(3.72)	
Va	99	222–225	42.51	3.86	4.93	617
			(42.35)	(3.92)	(4.94)	(567.24)
Vb	91	271–272	37.00	2.98	5.22	
			(36.95)	(3.11)	(5.39)	
Vc	90	259–260	31.63	2.70	4.47	
			(31.56)	(2.65)	(4.60)	

[a] All compounds decomposed with or without melting.

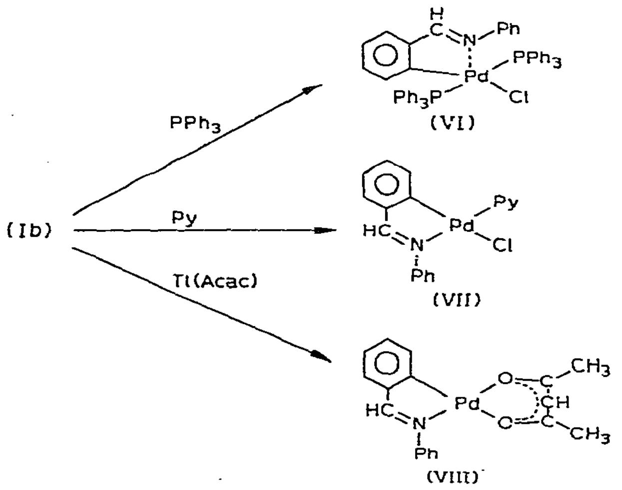
[b] Contained one CH_2Cl_2 per molecule, which was found in its proton NMR spectra at δ 5.27.

chloroform, slightly soluble in benzene, and insoluble in alcohol and n-hexane. On the other hand, halogen-bridged complexes are insoluble in almost all organic solvents.

The proton NMR spectrum of complex (Ia) shows a singlet at 7.61 (CH=N, 1H), a multiplet at 6.6–7.2 (aromatic-H, 9H) and a singlet at δ 1.79 (OC(O)CH_3, 3H). As reported[10], the chemical shift (δ 7.61) of an azomethine proton indicates that the coordination to palladium is established through the lone pair of nitrogen and not the C=N double bond.

As shown in Table 1, the acetato-bridged complexes exhibit two strong IR absorptions at ca. 1570 and 1410 cm^{-1} due to bridging acetato-groups[11]. The ν(C=N) frequencies are shifted to lower wavelengths by about 40 cm^{-1} in comparison with the corresponding frequencies of the starting Schiff bases, also indicating that nitrogen is coordinated to palladium through its lone pair[5,12]. The strong δ(CH) absorptions at ca. 720 cm^{-1}, which are characteristic of *ortho*-substituted aromatic rings[13], are observed in the complexes prepared, though there were no absorptions reported in the above area in the Molnar–Orchin complexes. Finally, two ν(PdCl) absorptions are found in each chloro-bridged complex; this is appropriate for the proposed structure[14].

The halogen-bridged complexes react with triphenylphosphine, pyridine and thallium acetylacetonate to give the expected products. For example, complexes (VI), (VII) and (VIII) are obtained from complex (Ib). That complex (VI) exhibits a ν(C=N) absorption at 1617 cm^{-1} compared with that (1637 cm^{-1}) of *N*-phenylbenzaldimine indicates the presence of the weak interaction of the azomethine bond with palladium.



EXPERIMENTAL

Melting points were determined on a Yanagimoto micro stage apparatus and are uncorrected. IR spectra (Nujol mulls) were recorded on a Nippon Bunko Model DS-403G spectrometer. Calibration was against polystyrene or water vapor. The proton NMR spectra were determined with a JEOL-60HL spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Molecular weights were determined with a Mechrolab Model 301A vapor pressure osmometer in a chloroform solution.

Materials

N-Phenylbenzaldimine and related compounds were prepared in the usual manner and recrystallized or distilled before use. Dichlorobis(benzonitrile)palladium(II) and palladium(II) acetate were prepared according to the reported procedures[15,16]. Methanol was dried by refluxing with magnesium ribbon and distilled.

Reaction of N-phenylbenzaldimine with dichlorobis(benzonitrile)palladium(II)

According to the method of Molnar and Orchin[6], we obtained yellow crystals (1.14 g) by the reaction between N-phenylbenzaldimine (1.81 g, 10 mmoles) and dichlorobis(benzonitrile)palladium(II) (0.77 g, 2 mmoles) in methanol (400 ml). These were suspended in dichloromethane (20 ml) and filtered to give dichlorodianilinepalladium(II) (1.00 g, 69%), m.p. 256–275° (dec.). IR spectrum: 3280, 3200, 3170(sh), and 3125($\nu(NH_2)$), 1602($\delta(NH_2)$), 1585(ν(C=C)), 760, 752, 747, and 685 cm^{-1} (δ(C–H)). Found: C, 40.13; H, 3.99; N, 8.18. $C_{12}H_{14}N_2PdCl_2$ calcd.: C, 39.64; H, 3.89; N, 7.71%.

The filtrate was concentrated and n-hexane was added to give dichlorobis(N-phenylbenzaldimine)palladium(II) as yellow crystals (0.12 g, 6%), m.p. 252–268° (dec.). IR spectrum: 1610(ν(C=N)), 1584 cm^{-1} (ν(C=C)). Found: C, 58.13; H, 4.21; N, 5.61; Cl, 13.41. $C_{26}H_{20}N_2PdCl_2$ calcd.: C, 57.75; H, 4.11; N, 5.18; Cl, 13.11%. When this compound was treated with triphenylphosphine, dichlorobis(triphenylphosphine) palladium(II) was isolated and N-phenylbenzaldimine was detected by thin layer chromatography.

In the same way, the reaction between N-phenylacetophenoneketimine and dichlorobis(benzonitrile)palladium(II) gave dichlorodianilinepalladium(II) in 82% yield. Reaction between N-(p-tolyl)benzaldimine and dichlorobis(benzonitrile)palladium(II) yielded two complexes.

Dichlorodi-p-toluidinepalladium(II); m.p. 275–285° (dec.); IR spectrum: 3280, 3205, 3170(sh), and 3120($\nu(NH_2)$), 814 and 743 cm^{-1} (δ(CH)). Found: C, 43.18; H, 4.55; N, 7.26. $C_{14}H_{18}N_2PdCl_2$ calcd.: C, 42.93; H, 4.64; N, 7.15%.

Dichlorobis(N-(p-tolyl)benzaldimine)palladium(II); m.p. >300°; IR spectrum: 1615(ν(C=N)), 1593 cm^{-1} (ν(C=C)). Found: C, 59.38; H, 4.56; N, 5.00. $C_{28}H_{26}N_2PdCl_2$ calcd.: C, 59.21; H, 4.62; N, 4.93%.

Preparation of di-μ-acetatobis(2,N-dihapto-N-phenylbenzaldimine)dipalladium(II) (Ia) and related complexes

When a solution of N-phenylbenzaldimine (1.90 g, 10.5 mmoles) and palladium(II) acetate (2.15 g, 10 mmoles) in acetic acid (50 ml) was heated, the color of the reaction mixture changed from dark red to yellow. After refluxing for 30 min, the reaction mixture was cooled, diluted with water, and extracted with dichloromethane. The extract was concentrated and chromatographed on silica gel (50 g). Complex (Ia) was eluted with dichloromethane containing 1% ethanol and recrystallized from dichloromethane/n-hexane to give yellow crystals (3.10 g, 96%).

Related complexes were prepared in a similar way from N-phenylacetophenoneketimine, N-phenylbenzophenoneketimine, N-(p-tolyl)benzaldimine and N-methylbenzaldimine.

IR data and yields, melting points, and analyses are summarized in Tables 1 and 2.

Preparation of halogen-bridged complexes

To a solution of acetato-bridged complexes in acetone was added an aqueous solution of sodium chloride or bromide, whereupon yellow solids were deposited. They were filtered, washed with water and dried.

IR data and yields, melting points, and analyses are summarized in Tables 1 and 2.

Preparation of complex (VI)

A yellow solution was obtained on adding triphenylphosphine (180 mg) to a suspension of di-μ-chlorobis(2,*N*-*dihapto*-*N*-phenylbenzaldimine)dipalladium(II)(Ib) (100 mg) in acetone (2 ml). Addition of n-hexane to the solution gave yellow crystals (257 mg, 98 %), changing to white at 105–120° and melting at 175–185°. This complex was found, from the molecular weight, to be completely dissociated in solution. IR spectrum: 1617 cm^{-1} (ν(C=N)). Found: C, 69.56; H, 5.07; mol. wt., 437. $C_{49}H_{40}NP_2$-PdCl calcd.: C, 69.50; H, 4.77 %; mol. wt., 846.69.

Preparation of complex (VII)

To a suspension of complex (Ib) (100 mg) in dichloromethane (1 ml) was added pyridine (0.1 ml). The resulting solution was evaporated and the residue was recrystallized from dichloromethane/n-hexane to give pale yellow needles (110 mg, 88 %), m.p. 291–292° (dec.). Found: C, 53.93; H, 3.85; N, 6.96. $C_{18}H_{15}N_2PdCl$ calcd.: C, 53.88; H, 3.78; N, 6.98 %.

Preparation of complex (VIII)

A suspension of complex (Ib) (322 mg, 0.5 mmole) and thallium acetylacetonate (606 mg, 2 mmoles) in dichloromethane (10 ml) was stirred for 1 h at room temperature. The mixture was passed through a short silica gel column with dichloromethane. The yellow fraction was evaporated and the residue was recrystallized from dichloromethane/n-hexane to give yellow crystals (360 mg, 93 %), m.p. 187–190°. IR spectrum: 1567 and 1512 cm^{-1} (ν(CO)). NMR spectrum: δ 8.03 (singlet, CH=N, 1H), 7.62–6.86 (multiplet, aromatic-H, 9H), 5.26 (singlet, CH, 1H), 2.04 (singlet, CH_3, 3H), and 1.82 (singlet, CH_3, 3H).

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