ORGANIC SYNTHESES BY MEANS OF NOBLE METAL COMPOUNDS XXXIII*. CARBONYLATION OF AZOBENZENE–PALLADIUM CHLORIDE COMPLEXES

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Various olefinic complexes of palladium chloride react with carbon monoxide to form carbonyl compounds, and they are useful intermediates in organic syntheses. We have shown that olefin π-complexes react with carbon monoxide to give β-chloroacyl chlorides at room temperature[2], and π-allylic complexes to afford β,γ-unsaturated acid derivatives[3]. Furthermore, the carbonylation of amines can be carried out in the presence of palladium chloride to give isocyanates[4], substituted ureas, oxamides and formamides[5]. In these carbonylation reactions, it is assumed that a σ-bond between palladium and carbon or nitrogen atom should be formed as a prerequisite of the carbonylation. The palladium σ-bonds with carbon or nitrogen atom are very reactive toward carbon monoxide, and undergo carbon monoxide insertion. In this paper, the preparation of palladium chloride complexes of several azobenzenes and the carbonylation of the complexes are reported.

The reaction of azobenzene with palladium chloride to form a stable complex was reported by Cope and Siekman, who established that the complex involves a carbon–palladium σ-bond[6]. The complex formation is very interesting in view of the fact that substitution reaction at the benzene ring with palladium chloride to form the stable palladium–carbon σ-bond takes place smoothly under very mild conditions. In general, palladium–carbon σ-bonds are not stable without appropriate stabilizing ligands and are not formed easily. It is expected that the azobenzene complex, having the palladium–carbon σ-bond, is a promising compound for the introduction of carbon monoxide on the benzene ring.

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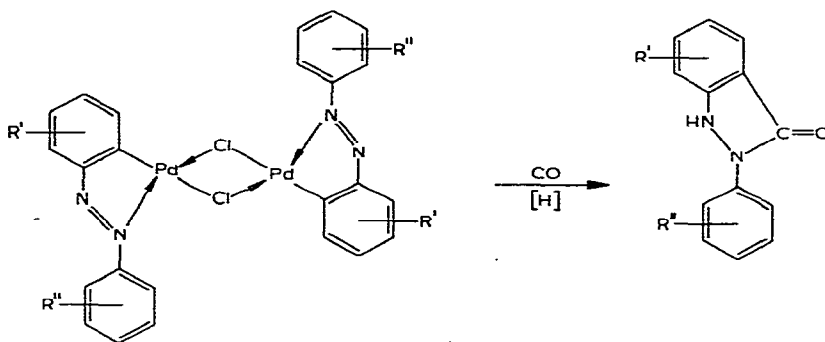
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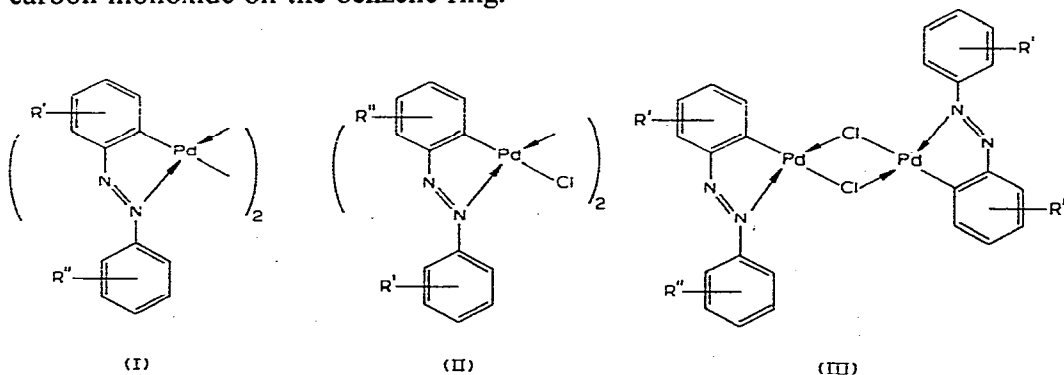
* For Part XXXII see ref. 1.

TABLE 1

SUBSTITUTED AZOBENZENE–PALLADIUM CHLORIDE COMPLEXES

Azo compound	Complex	M.p. (°C)	Yield (%)	Color	Analyses found (calcd.) (%)				
					C	H	N	Cl	Pd
4,4'-Dimethylazobenzene	$(C_{14}H_{13}N_2ClPd)_2$	255–257	99	orange	47.73 (47.89)	3.76 (3.73)	8.07 (7.98)	10.41 (10.10)	30.2 (30.3)
3,3'-Dimethylazobenzene	$(C_{14}H_{13}N_2ClPd)_2$	258–260	97	red	47.48 (47.89)	3.74 (3.73)	7.95 (7.98)	10.41 (10.10)	31.6 (30.3)
2,2'-Dimethylazobenzene	$(C_{14}H_{13}N_2ClPd)_2$	253–255	89	orange	47.63 (47.89)	3.81 (3.73)	7.75 (7.98)	10.26 (10.10)	30.6 (30.3)
4,4'-Dichloroazobenzene	$(C_{12}H_7N_2Cl_3Pd)_2$	>250	51	orange	37.11 (36.77)	1.86 (1.80)	7.04 (7.15)	27.18 (27.14)	26.9 (27.1)
3,3'-Dichloroazobenzene	$(C_{12}H_7N_2Cl_3Pd)_2$	>250	78	red	36.92 (36.77)	1.95 (1.80)	7.14 (7.15)	27.10 (27.14)	25.9 (27.1)
2,2'-Dichloroazobenzene	$(C_{12}H_7N_2Cl_3Pd)_2$	>250	66	orange	36.88 (36.77)	1.80 (1.80)	7.24 (7.15)	27.22 (27.14)	27.1 (27.1)
4-Methoxyazobenzene	$(C_{13}H_{11}N_2OClPd)_2$	237–240	98	red	44.39 (44.22)	3.20 (3.14)	7.79 (7.93)	10.01 (10.04)	31.1 (30.1)
4-Methylazobenzene	$(C_{13}H_{11}N_2ClPd)_2$ [a]		89	red	46.37 (46.32)	3.37 (3.29)	8.05 (8.31)	10.60 (10.52)	31.5 (31.6)
4-Chloroazobenzene	$(C_{12}H_8N_2Cl_2Pd)_2$ [a]		87	orange-red	40.76 (40.31)	2.41 (2.26)	7.98 (7.84)	19.75 (19.83)	29.0 (29.8)

[a] The mixture of the three possible complexes.

The complex formation with several symmetrically and asymmetrically substituted azobenzenes was carried out by applying the method of Cope and Siekman with some modifications. Some complexes prepared are shown in Table 1. The structure of the symmetrically substituted azobenzene complexes was established by Cope and Siekman. On the other hand, there are three possible structures, (I), (II) and (III), for the complexes of asymmetrically substituted azobenzenes, depending on which benzene ring is attacked by the palladium. The orientation of the σ-bond formation was determined by the carbonylation, followed by chemical degradations as described later.

Then carbonylation reaction of the complexes was attempted. The reaction proceeded smoothly under mild conditions in protic solvents such as alcohol or water to give 2-aryl-3-indazolinones with separation of metallic palladium in high yields. This reaction is a very good synthetic method of substituted 2-aryl-3-indazolinones. The substituted indazolinones described in this paper are all new compounds. For the formation of the indazolinone, a proton source is essential. The reaction proceeds even at room temperature showing that the σ-bond is very reactive toward carbon monoxide as expected. Although the complex is insoluble in water, the car-

bonylation proceeded satisfactorily in water. The results of the carbonylation of the complexes under various conditions are shown in Table 2.

For asymmetrically substituted azobenzenes, there are two possible orientations of the σ-bond formation, and hence the products of the carbonylation should be different. In other words, the orientation of the initial σ-bond formation can be determined by studying the structure of the carbonylation products, because the ring σ-bonded to the palladium is attacked by carbon monoxide. The determination of the
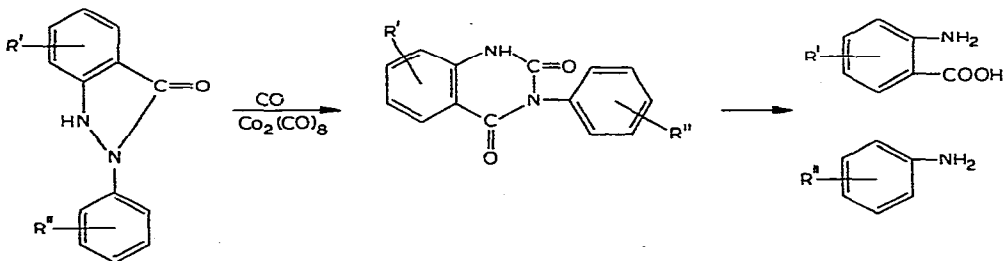
TABLE 2

CARBONYLATION OF THE COMPLEXES

Complex	Solvent	CO (atm)	Temp. (°C)	Time (h)	Indazolinone	M.p. (°C)	Yield (%)	Analyses found (calcd.) (%) C	H	N	Cl
Azobenzene	EtOH	150	100	5	$C_{13}H_{10}N_2O$	204–205	97	74.07 (74.27)	5.07 (4.79)	13.00 (13.33)	
Azobenzene	EtOH	30	100	5	$C_{13}H_{10}N_2O$	204–205	79				
Azobenzene	EtOH	150	20	16	$C_{13}H_{10}N_2O$	204–205	72				
Azobenzene	H_2O	100	100	3	$C_{13}H_{10}N_2O$	204–205	55				
Azobenzene	C_6H_6	150	100	5	$C_{13}H_{10}N_2O$		0				
4,4'-Dimethylazobenzene	EtOH	150	100	5	$C_{15}H_{14}N_2O$	234–236	97	75.42 (75.60)	6.12 (5.92)	11.87 (11.76)	
3,3'-Dimethylazobenzene	EtOH	150	100	5	$C_{15}H_{14}N_2O$	209–211	97	75.59 (75.60)	6.13 (5.92)	11.88 (11.76)	
2,2'-Dimethylazobenzene	EtOH	150	100	5	$C_{15}H_{14}N_2O$	168–169	97	75.85 (75.60)	6.00 (5.92)	11.65 (11.76)	
4,4'-Dichloroazobenzene	EtOH	100	100	5	$C_{13}H_8N_2OCl_2$	210–213	96	55.98 (55.94)	2.93 (2.89)	9.86 (10.04)	25.45 (25.41)
3,3'-Dichloroazobenzene	EtOH	150	100	5	$C_{13}H_8N_2OCl_2$	210–213	86	56.19 (55.94)	2.96 (2.89)	9.88 (10.04)	25.51 (25.41)
2,2'-Dichloroazobenzene	EtOH	100	100	5	$C_{13}H_8N_2OCl_2$	197–199	96	55.93 (55.94)	2.86 (2.89)	9.97 (10.04)	25.48 (25.41)
4-Methoxyazobenzene	EtOH	85	100	5	$C_{14}H_{12}N_2O_2$	199–201	94	70.18 (69.99)	5.08 (5.03)	11.72 (11.66)	
4-Methylazobenzene	EtOH	88	100	5	$C_{14}H_{12}N_2O^a$		84	74.69 (74.99)	5.48 (5.38)	12.57 (12.49)	
4-Chloroazobenzene	EtOH	100	100	3	$C_{13}H_9NOCl^a$		97	63.53 (63.81)	3.71 (3.68)	11.55 (11.45)	14.46 (14.50)

^{a} The mixture of the two possible indazolinones.

structure of the indazolinones was carried out in the following way. It is known that the indazolinone can be carbonylated further to give substituted quinazolinedione by the catalytic action of cobalt carbonyl[7]. The hydrolysis of the quinazolinedione affords aniline and anthranilic acid derivatives. The structural determination of the aniline and anthranilic acid derivatives conclusively establishes the orientation of the initial σ-bond formation.

Thus, from the quinazolinedione obtained by the carbonylation of 4-methylazobenzene complex, aniline, rather than toluidine was obtained as a main product (aniline/toluidine, 3 : 1, gas chromatographically determined). The result shows that the σ-bond formation with palladium took place mainly with the benzene ring having the methyl group. With 4-chloroazobenzene complex, a larger amount of p-chloroaniline was obtained than aniline(p-chloroaniline/aniline, 3 : 1) showing that the σ-bond formation took place predominantly at the unsubstituted benzene ring of 4-chloroazobenzene. On the other hand, the carbonylated product of the complex of 4-methoxyazobenzene afforded only aniline by the degradation and no anisidine was detected. From these results, it can be concluded that the σ-bond formation is an electrophilic substitution of palladium chloride on the benzene ring. Since the substitution of the palladium takes place at the meta position of the substituent, the effect of the substituents is explained by inductive effects. Thus methoxy and methyl groups have strong influence on the orientation of the σ-bond formation. Comparative studies on the effect of the substituents at the positions 3 and 4 seem to be interesting and they will be the topics of further studies.

The mechanism of the carbonylation is not completely clear and further mechanistic studies are in progress. Tentatively, the following mechanism can be given. The first step is the coordination of carbon monoxide with the splitting of the bridged structure. Then follows the insertion of carbon monoxide at the σ-bond to give an acyl–palladium bond. The final step seems to be the insertion of the $-N=N-$
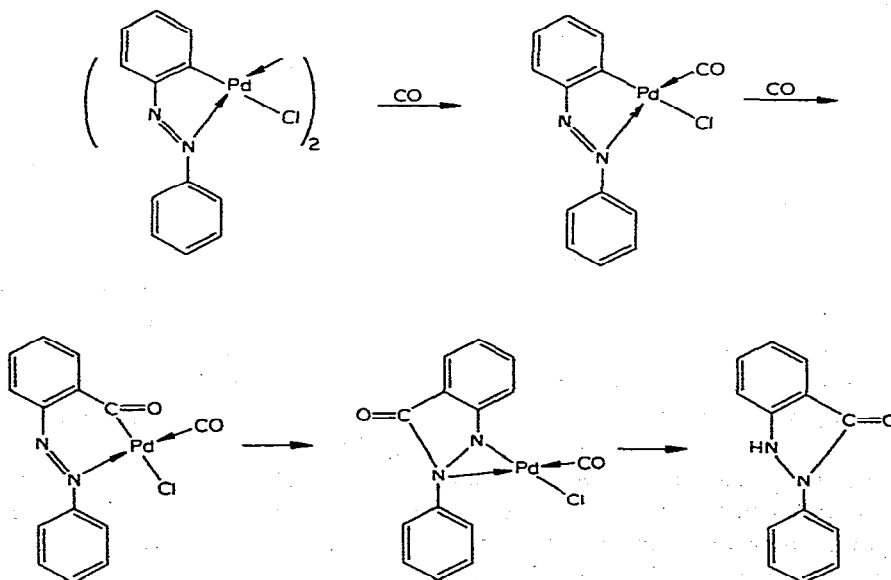
bond into the palladium–acyl bond, followed by hydrogenolysis of the palladium–nitrogen bond.

The carbonylation of azobenzene with cobalt carbonyl to give indazolinone is known, but no mechanism was given for the reaction[7]. The present studies show that the introduction of carbon monoxide at the benzene ring is possible if any kind of carbon–metal σ-bonds is formed. Therefore, it is highly probable that an azobenzene–cobalt carbonyl complex having a carbon–cobalt bond at the benzene ring is formed before the introduction of carbon monoxide at the benzene ring in the cobalt carbonyl catalyzed carbonylation.

EXPERIMENTAL

Only typical examples of the complex formation and the carbonylation reactions are described below.

Preparation of azobenzene complex

An ethanolic solution containing azobenzene (5.5 g/200 ml) was added to sodium chloropalladate (9.0 g) in ethanol. On mixing, an orange precipitate appeared immediately. After standing for 24 h at room temperature, the orange precipitate was collected by filtration, washed with ethanol and water, and dried to give 9.5 g of azobenzene–palladium chloride complex, m.p. 275–280° (dec.)(lit.[6] 279–281°). The infrared spectrum (KBr pellet) of this complex reveals major absorptions at 3050, 1575, 1450, 1395, 1300, 1240, 760, 750, 705, and 695 cm^{-1}: ultraviolet spectrum [mμ(ε)] in chloroform: λ_{max}240(41,300), 327(23,600).

Preparation of 4,4'-dimethylazobenzene complex

Sodium chloropalladate (3.0 g) was dissolved in ethanol (50 ml) and an ethanolic solution of 4,4'-dimethylazobenzene (2.1 g) was added. The mixture was left at a room temperature for 24 h, during which the complex deposited as orange crystals. The complex was collected by filtration, washed with ethanol and water, and dried in a dessicater. Although the complex is difficultly soluble in ordinary organic solvents, it is practically pure for further reactions. The infrared spectrum (KBr pellet): 3000, 2900, 1600, 1575, 1385, 1310, 1270, 1255, 815, and 810 cm^{-1}: ultraviolet spectrum [mμ(ε)] in chloroform: λ_{max}247(43,900), 345(25,600). The other complexes prepared are shown in Table 1.

Carbonylation reaction of the complexes

1. *Carbonylation of azobenzene complex in ethanol.* The complex (1.6 g) was placed in a glass vessel equipped with a gas-inlet capillary with 30 ml of ethanol. The vessel was set in a 200 ml stainless steel autoclave. Carbon monoxide was introduced (150 atm) and the reaction was carried out at 100° for 5 h. After the reaction, precipitated palladium was separated by filtration and the filtrate was concentrated to give 1.0 g of 2-phenyl-3-indazolinone, m.p. 204–205° (lit.[7] 204°).

2. *Carbonylation of azobenzene complex in water.* The complex (1.6 g) suspended in water (50 ml) was carbonylated at 100° under pressure (CO, 100 atm) for 3 h. After the reaction, water was removed by filtration, and the solid was recrystallized from ethanol to give 0.58 g of 2-phenyl-3-indazolinone.

Carbonylation and structure determination of 4-methoxyazobenzene complex

4-Methoxyazobenzene complex (1.2 g) was carbonylated in ethanol in the same way as shown above, and the methoxy-substituted indazolinone (0.78 g) was obtained, m.p. 199–201°. The indazolinone (1.0 g) was carbonylated in benzene (20 ml) in the presence of cobalt carbonyl (0.3 g) at 230–235° for 3 h under pressure (CO, 150 atm). The methoxy-substituted quinazolinedione (0.2 g) thus obtained was hydrolyzed by heating with 20% potassium hydroxide solution. After hydrolysis, the solution was extracted with ether, and the ethereal solution was subjected to gas chromatographic analysis (Apiezon-L 5% KOH, Cellite-545, carrier gas helium 40 ml/min at 141°). Only aniline was detected.

SUMMARY

Palladium chloride complexes of symmetrically and asymmetrically substituted azobenzenes have been prepared. The carbonylation of the complexes in protic solvents affords 2-aryl-3-indazolinones in a high yield. It was found by degradative work of the carbonylated products that when the asymmetrically substituted azobenzene was treated with palladium chloride, a palladium–carbon σ-bond is formed preferentially with the benzene ring having an electron donating group.

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