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THE COORDINATION-CATALYZED *ortho*-HALOGENATION OF AZOBENZENE

DARRYL R. FAHEY
Research and Development Division, Phillips Petroleum Company, Bartlesville, Oklahoma 74004 (U.S.A.)
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SUMMARY

Azobenzene is halogenated by chlorine and bromine selectively *ortho* to the azo group when its solutions are treated with the respective halogen in the presence of a palladium(II) catalyst. All possible *ortho*-chlorinated products are obtained, and 2,6,2′,6′-tetrachloroazobenzene is obtained as the major product upon exhaustive chlorination. The specificity for *ortho*-halogenation is derived from the interaction of the halogen with a carbon–metal σ-bonded intermediate, di-μ-halobis[2-(phenylazo)-phenyl]dipalladium(II) (I). Intermediates such as (I) were isolated from reaction mixtures and characterized by their far-IR spectra and their reactions with chlorine and triphenylphosphine.

INTRODUCTION

Recently, the field of homogeneous catalysis has been expanded by the discovery of palladium-assisted aromatic substitution reactions. The most prominent examples involve vinylations by olefins and substituted olefins[1], although nitro[2], acetoxy[2], and carboxyl[1] groups have also been introduced into benzene rings. These reactions are generally thought to proceed via σ-bonded arylpalladium intermediates, but, in most cases, the mode of formation of the arylpalladium species remains obscure. Most of the success in this area has been in the use of arylmercury salts to arylate palladium[3]. Unfortunately, this reaction, although catalytic in palladium, is stoichiometric with respect to mercury. To ensure a turnover of palladium in the catalytic reactions, the palladium must be maintained in a +2 oxidation state. This is usually achieved by the use of cupric halides as oxidants, themselves being easily reoxidized.

We recently reported preliminary results concerning a palladium-catalyzed chlorination reaction of azobenzene[4]. Azobenzene is a particularly well suited substrate for the study of coordination-catalyzed aromatic substitution reactions, since it is capable of undergoing direct ring substitution by Pd^{II} and Pt^{II} chlorides[5]. We report now a more detailed description of this reaction.

RESULTS AND DISCUSSION

Stirring a dioxane/water solution of azobenzene and $PdCl_2$ at 85–90° resulted in the formation of a red-maroon solid with the concurrent evolution of HCl. Upon slow introduction of gaseous chlorine into the solution, the solid dissolved, and the solution turned orange. Chlorine addition was continued at a rate that maintained the solution between maroon and orange over 16 h. The azobenzene derived products were obtained as an orange-red solid by extraction from the reaction mixture and chromatography on alumina. Analysis of the solid by GLC revealed that it was composed of 2-chloroazobenzene (12% of mixture, 8% yield), 2,6-dichloroazobenzene (22%, 15%), 2,2'-dichloroazobenzene (30%, 20%), 2,6,2'-trichloroazobenzene (33%, 22%), and 2,6,2',6'-tetrachloroazobenzene (3%, 2%). Spectra of each component were obtained on samples collected by preparative GLC. 2-Chloroazobenzene and 2,2'-dichloroazobenzene were readily identified upon examination of their IR and mass spectra. In addition, the IR spectrum of 2,2'-dichloroazobenzene is identical to the Sadtler spectrum for the same compound. The IR and mass spectra of the other three products are consistent with the assigned structures as well as with the corresponding 2,3-polychlorinated isomers. At higher concentrations of palladium, the mono-, di-, and trichloroazobenzene were further converted to 2,6,2',6'-tetrachloroazobenzene, since the GLC peak with the longest retention time increased as the reaction progressed at the expense of the peaks with shorter retention times. When a 1/1 molar ratio of palladium and azobenzene, in the form of di-μ-chlorobis[2-(phenylazo)phenyl]-dipalladium(II) (I), was treated with chlorine for 60 h at 85°, 2,6,2',6'-tetrachloroazobenzene was obtained as the major product in a 39% recrystallized yield. The assignment of its structure was confirmed upon careful examination of its 60 MHz proton NMR spectrum (Fig. 1). The complexity of the spectrum precludes a simple first-order analysis. However, a NMRIT computer simulated A_2B spectrum with $\Delta H(A)H(B)$ 12.2 Hz, $J(A-B)$ 8.0 Hz, and $J(A-A)$ 1.5 Hz gave very good agreement with the ob-

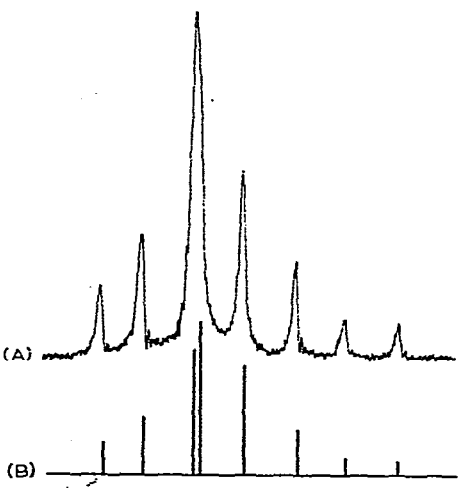


Fig. 1. (A) 60 MHz proton NMR spectrum (CCl_4) of 2,6,2',6'-tetrachloroazobenzene; (B) Computer simulated A_2B NMR spectrum.

served spectrum (Fig. 1). The chemical shifts H(A) τ 2.64 and H(B) τ 2.84 are accurate within 1 Hz and the J values within 0.1 Hz. This spectrum is only consistent with the symmetrical 2,6,2',6'-tetrachloroazobenzene structure. An independent synthesis of this compound from 2,6-dichloroaniline using the oxidative coupling technique described in Organic Synthesis for the conversion of *p*-aminoacetanilide to 4,4'-diacetamidoazobenzene[6] was unsuccessful. A similar reaction with 2,3-dichloroaniline afforded a low yield of 2,3,2',3'-tetrachloroazobenzene, m.p. 199–201°, which was not identical to the tetrachloroazobenzene described above.

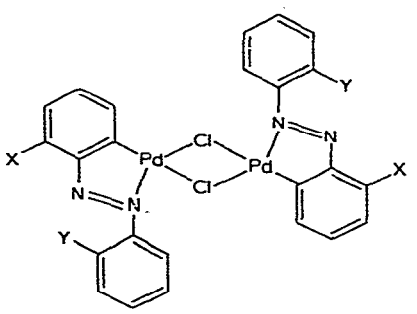
The selectivity for *ortho*-chlorination and the reaction rate are improved when HCl is swept from the reaction zone by passing nitrogen through the solution. The HCl presumably retards the formation of the [2-(phenylazo)phenyl]palladium intermediate and promotes a competing azobenzene chlorination[7].

To establish true catalysis by palladium, the initial reaction described was repeated with $PdCl_2$ absent. The azobenzene derived product mixture from this reaction was composed of azobenzene (16%), 4-chloroazobenzene (71%, includes a small amount of 2-chloroazobenzene), and 4,4'-dichloroazobenzene (13%). A similar preference for *para*-chlorination of azobenzene had been observed previously in chlorinations conducted in aqueous acetic acid[7].

Bromination could only be effected in stoichiometric reactions. Thus treatment of di-μ-bromobis[2-(phenylazo)phenyl]dipalladium(II) (II) with bromine afforded 2-bromoazobenzene. Catalytic reactions failed presumably because the HBr formed was not expelled from the reaction solution. Passing nitrogen through the solution was even ineffective at removing HBr. Like HCl, the HBr apparently inhibited formation of (II) and, more seriously, catalyzed the bromination of azobenzene[7] and gave a mixture of several unidentified products.

Although potassium tetrachloroplatinate(II) and azobenzene form the [2-(phenylazo)phenyl]platinum analogue of (I), attempts at catalyzing the chlorination of azobenzene by either platinum(II) chlorides or by di-μ-chlorobis[2-(phenylazo)-phenyl]diplatinum(II) have been unsuccessful (one attempt is included in the experimental section). The organoplatinum complex retains the carbon–metal σ-bond upon treatment with chlorine. A remarkable resistance to bromine attack on a Pt–C bond in a related complex has been previously described[8].

Proof that the mechanism of the *ortho*-chlorination reaction proceeds via complex (I) as an intermediate was obtained by the isolation of (I) from reaction mixtures prior to chlorine addition. Furthermore, at later stages of the reaction, a 4/1

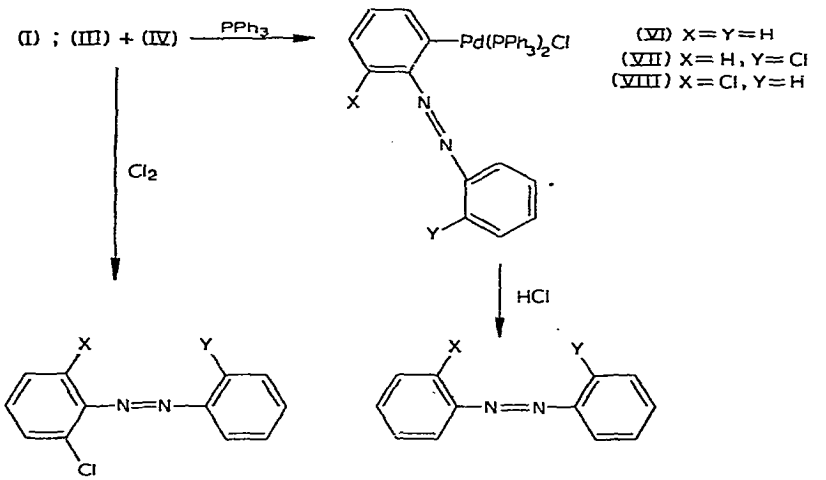


(I) X=Y=H
(III) X=H, Y=Cl
(IV) X=Cl, Y=H
(V) X=Y=Cl

mixture of (III) and (IV) was isolated. Complexes (III) and (IV) are intermediates in the formation of the two dichloroazobenzenes. Reactions which aided in the identification of these organopalladium complexes are illustrated in Scheme 1. Reaction of (I) or the mixture of (III) and (IV) with triphenylphosphine afforded complex (VI) and

SCHEME 1

REACTIONS OF 2-(PHENYLAZO)PHENYLPALLADIUM(II) COMPLEXES



a mixture of (VII) and (VIII), respectively. Treatment of these new complexes with anhydrous HCl yielded azobenzene from (VI) and 2-chloroazobenzene from the mixture of (VII) and (VIII). A comparison of these reactions allows the assignment of one and only one chloro substituent in either a 3- or a 2'-position of the azobenzene moiety in (III) and (IV), but does not distinguish between these positions. Upon treatment with chlorine, (I) gave 2-chloroazobenzene, and the mixture of (III) and (IV) yielded a 4/1 mixture of 2,2'-dichloroazobenzene and 2,6-dichloroazobenzene. Therefore, 80% of the 2-(phenylazo)phenyl groups in the mixture of (III) and (IV) possess the chloro substituent in the 2'-position with the remaining 20% having the chloro group in the 3-position.

The far-infrared spectra of the chloro-bridged [2-(phenylazo)phenyl]palladium(II) complexes merit special comment. The spectra of (I), of the mixture of (III) and (IV), and of di-μ-chlorobis[2-(2-chlorophenylazo)-3-chlorophenyl]dipalladium(II) (V), prepared from 2,2'-dichloroazobenzene and $PdCl_2$, are given in Table 1. Each complex exhibits two absorptions between 200–300 cm^{-1} which may be assigned to bridging Pd–Cl stretching vibrations associated with an asymmetric Pd_2Cl_2 unit. The assignments shown coincide well with frequencies for the same vibrations in structurally related complexes. In chloro-bridged palladium complexes possessing chelating ligands bound to palladium by a carbon–metal σ-bond and by an olefin–metal bond, two Pd–Cl stretching vibrations at 272–284 and 222–242 cm^{-1} were observed[9].

The chloro substituents in complexes (III) and (V) are in positions which allow specific assignments to be made for the Pd–Cl stretching vibrations *trans* to carbon or nitrogen. The electron-withdrawing chloro-substituent *ortho* to nitrogen in the

TABLE 1

INFRARED ABSORPTIONS (210–375 cm^{-1}) OF THE CHLORO-BRIDGED [2-(PHENYLAZO)PHENYL]PALLADIUM(II) DERIVATIVES

Band assignments	(I)	(III)+(IV)[a]	(V)	(I)[b]
ν(Pd–Cl) (*trans* to C)	237 m	235 m	247 m	262 s
ν(Pd–Cl) (*trans* to N)	266 s	282 s, 262 (sh)	280 s	337 s
Other absorptions	323 m	326 ms	330 m	233 m
	344 m	356 mw	367 m	252 (sh)
	373 m			268 (sh)
				320 m
				368 m

[a] The spectrum is predominantly that of (III) since it accounts for 80% of the mixture. The shoulder at 262 cm^{-1} is believed to be associated with (IV). The weak absorption expected at ca. 247 cm^{-1} for (IV) was not distinguishable. [b] Frequencies and assignments taken from ref. 11.

benzene ring not bonded to palladium, as in (III) and (V), decreases the σ-donor ability of the nitrogen bound to palladium, thereby decreasing its *trans* influence and increasing the stretching frequency of its *trans* Pd–Cl bond. This is indeed observed as the strong absorption band at 266 cm^{-1} in (I) shifts to 282 and 280 cm^{-1}, respectively, for (III) and (V). Likewise, substitution of chlorine into the benzene ring bonded to palladium decreases the *trans* influence of the carbon σ-bonded to palladium and increases the stretching frequency of its *trans* Pd–Cl bond. In complex (V), which bears a chloro substituent *meta* to palladium, the lower frequency bands at 237 and 235 cm^{-1} in (I) and (III), respectively, shift to 247 cm^{-1}. A decreased *trans* influence of a σ-bonded vinyl group with chlorine substitution has previously been observed in complexes of the type *trans*-$(Ph_3P)_2Pd(R)Cl$[10].

The far-IR spectrum of (I) has been reported elsewhere[11], and the absorption frequencies and assignments are reproduced in Table 1 for comparison. For the most part, the two spectra of (I) agree except that the earlier reported absorptions are displaced to lower wave numbers by 3–7 cm^{-1}, and their absorption at 337 cm^{-1} appears more intense than our corresponding absorption at 344 cm^{-1}. Different assignments have been made for the Pd–Cl stretching vibrations, but only the present assignments are compatible with the observed effect of varying *trans* influences. The Pd–Cl stretching vibrations in these complexes are likely coupled to one another and to other molecular vibrations, but the independent variation of frequencies for each vibration with its *trans* ligand suggests that any such coupling is small.

The probable mechanism of the aromatic substitution reaction of azobenzene with palladium has been discussed in detail by Parshall[12]. The reaction is best described as a classical aromatic electrophilic substitution of a *N*-coordinated azobenzene. In accord with this mechanism, we find azobenzene to be more reactive than any of its *ortho*-chlorinated derivatives. Chlorination of a 30/1 molar ratio of azobenzene and $PdCl_2$ for 35 h afforded a product mixture comprising azobenzene (26%), 2-chloroazobenzene (68%), 2,6-dichloroazobenzene (2%), and 2,2′-dichloroazobenzene (3%). The expected deactivation of the ring bearing a chlorine substituent as well as the decreased σ-donor ability of the nitrogen *ortho* to chlorine (coordination of this nitrogen to palladium is necessary for substitution of the opposite ring) result in a decreased reactivity of azobenzene after *ortho*-chlorination. The decrease in the σ-

TABLE 2

HALOGENOLYSIS PRODUCTS FROM (I) AND (II)

Reactants	Products (%)		
	Azobenzene[a]	2-Chloroazobenzene	2-Bromoazobenzene
(I) + Cl_2	+	100	
(II) + Cl_2	+	84	16
(I) + Br_2		2	98
(II) + Br_2			100

[a] + Denotes a small amount of azobenzene was present in the product mixture but is excluded from the percentages.

donor capability of nitrogen *ortho* to chlorine was also supported by the frequency shifts of Pd–Cl stretching vibrations *trans* to nitrogen in (III) and (IV) discussed earlier. This reactivity difference is an advantage when a 2-chloroazobenzene is desired, since the azobenzene reactant will undergo halogenation more rapidly than the product.

A general mechanism for the halogenolysis of a transition-metal–carbon bond has not yet been defined. An oxidative-addition of the halogen to the metal followed by a reductive-elimination of the product alkyl halide has been observed with a methylplatinum complex[13]. Examination of the product distributions obtained upon bromination and chlorination of (I) and (II) (Table 2) suggests that at least part of the products could be formed via this type of mechanism. In entries 2 and 3, some of the halogen originally bound to palladium does appear in a haloazobenzene product. Further discussion or speculation about this mechanism must be reserved until additional data are obtained.

EXPERIMENTAL

Anhydrous palladium and platinum chlorides were purchased from K and K Laboratories. Potassium tetrachloroplatinate(II) was prepared by refluxing 0.60 g of potassium chloride with 1.06 g of platinum chloride in 50 ml of water until the solution became homogeneous. Other materials were commercially available samples generally used without further purification or were prepared by published methods.

Melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were run on Perkin–Elmer Infracord Model 137 (650–4000 cm^{-1}) and Perkin–Elmer Model 301 (200–450 cm^{-1}) spectrophotometers. The far-IR spectra (CsI wafers) were calibrated with water vapor and are accurate within ± 1 cm^{-1}. Relative intensities of absorptions below 300 cm^{-1} are not directly comparable to those above 300 cm^{-1} due to differences in sample thickness. Mass spectra were obtained on a CEC 21-110 high resolution instrument. The proton NMR spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The chlorinated azobenzenes were analyzed by GLC on a Hewlett–Packard Model 5750 gas chromatograph employing a flame-ionization detector in combination with a 6′ by 1/8″ 10% SE-30 on 60/80 Chrom P column at 225°. The preparative

GLC was done with a Hewlett–Packard Model 776 Prepmaster with a 80" by 3/4" 20% W-98 silicone oil column.

Chlorination of azobenzene catalyzed by palladium.

(*A*). A solution of 1.00 g (5.5 mmoles) of azobenzene and 0.20 g (1.1 mmoles) of $PdCl_2$ in 50 ml of dioxane and 25 ml of water was stirred at 85–90°. After the mixture turned maroon and a red solid had formed, chlorine gas was introduced into the solution through a gas-dispersion tube. The rate of chlorine addition was controlled to maintain the solution between orange and maroon. After 16 h, the reaction was terminated, and the mixture was extracted with 50 ml of ether. The extract was taken to dryness under vacuum, and the residue was chromatographed on alumina. The azobenzene derived products eluted together with 2% ether in pentane and were obtained as an orange-red solid (0.94 g). The solid was composed of five compounds, and a small amount of each was obtained in pure form by preparative GLC. The first component was 2-chloroazobenzene (12%). The major absorptions exhibited by its IR spectrum (neat) are at 3030, 1580, 1450, 1150, 1056, 770, 757, 717, and 684 cm^{-1}. Its NMR spectrum ($CDCl_3$) consists of a complex multiplet centered at τ 2.50. The mass spectrum (70 eV) possesses peaks for $C_{12}H_9ClN_2^{\ddagger}$, $C_6H_4ClN_2^+$, $C_6H_4Cl^+$, $C_6H_5N_2^+$, and $C_6H_5^+$. The second component was 2,6-dichloroazobenzene (22%). The major absorptions in its IR spectrum (KBr) are at 1560, 1425, 1145, 790, 770, 764, 726, and 684 cm^{-1}. Its NMR spectrum ($CDCl_3$) is composed of complex multiplets centered at τ 2.00, 2.43, and 2.73. The mass spectrum (70 eV) possesses peaks for $C_{12}H_8Cl_2N_2^{\ddagger}$, $C_6H_3Cl_2N_2^+$, $C_6H_3Cl_2^+$, $C_6H_5N_2^+$, and $C_6H_5^+$. The third component was 2,2'-dichloroazobenzene (30%). Its IR spectrum (KBr) is identical to Sadtler Spectrum No. 35372 for the same compound. Its NMR spectrum ($CDCl_3$) is a complex multiplet centered at τ 2.50. The mass spectrum (70 eV) possesses peaks for $C_{12}H_8Cl_2N_2^{\cdot}$, $C_6H_4ClN_2^+$, and $C_6H_4Cl^+$. The fourth component was 2,6,2'-trichloroazobenzene (33%). The major absorptions exhibited by its IR spectrum (KBr) are at 1560, 1450, 1425, 1055, 792, 773, 756, and 703 cm^{-1}. Its NMR spectrum ($CDCl_3$) consists of a complex multiplet centered at τ 2.60. The mass spectrum (70 eV) possesses peaks for $C_{12}H_7Cl_3N_2^{\ddagger}$, $C_6H_3Cl_2N_2^+$, $C_6H_4ClN_2^+$, $C_6H_3Cl_2^+$, and $C_6H_4Cl^+$. The last component was 2,6,2',6'-tetrachloroazobenzene (3%). The major absorptions in its IR spectrum (KBr) are at 1560, 1430, 1200, 1090, 917, 793, 770, 733, and 723 cm^{-1}. Its NMR spectrum is illustrated in Fig. 1. The mass spectrum (70 eV) possesses peaks for $C_{12}H_6Cl_4N_2^{\ddagger}$, $C_6H_3Cl_2N_2^+$, and $C_6H_3Cl_2^+$.

(*B*). Reaction (A) was repeated except 1.46 g (2.27 mmoles) of di-μ-chlorobis-[2-(phenylazo)phenyl]dipalladium(II)[5] was used as the source of azobenzene and palladium. Additionally, nitrogen was continuously passed through the solution. Analysis of the mixture by GLC at progressive stages of the reaction indicated that 2,6,2',6'-tetrachloroazobenzene was being formed at the expense of the other chlorinated azobenzenes. After 60 h, the azobenzene products were extracted from the mixture with ether. The extract was taken to dryness under vacuum, and the residue (0.98 g) was chromatographed on alumina. Recrystallization from methanol of the red solid eluted with 2% ether in pentane afforded 0.57 g (39%) of brown 2,6,2',6'-tetrachloroazobenzene, m.p. 93–94°. (Found: C, 45.1; H, 2.18. $C_{12}H_6Cl_4N_2$ calcd.: C, 45.03; H, 1.89%). The IR, NMR, and mass spectra are identical to those described above for the same compound. A small amount of a red solid, m.p. 82–116°, was ob-

tained from the mother liquors, and its mass spectrum is identical to that for 2,6,2',6'-tetrachloroazobenzene. Its IR is consistent with either 2,4,2',6'- or 2,5,2'6'-tetrachloroazobenzene.

(C). Reaction (A) was repeated with 0.20 g (1.0 mmole) of $PdCl_2$ and 5.60 g (30.8 mmoles) of azobenzene. After 35 h, the azobenzene products were isolated by extraction and chromatography as in (A), and the orange-red oil obtained was analyzed by GLC. The mixture was found to be composed of azobenzene (26%), 2-chloroazobenzene (68%), 2,6-dichloroazobenzene (2%), and 2,2'-dichloroazobenzene (3%).

Chlorination of azobenzene catalyzed by platinum

A solution of 1.00 g (5.5 mmoles) of azobenzene and 0.22 g (0.53 mmoles) of di-μ-chlorobis[2-(phenylazo)phenyl]diplatinum(II)[5] in 50 ml of dioxane and 10 ml of water was stirred at 85°. Upon passing nitrogen diluted chlorine into the mixture, the maroon solution turned orange. After 6 h, the reaction was terminated, and the mixture was analyzed by GLC. Only azobenzene was present in solution.

We have also observed that treating solutions of the [2-(phenylazo)phenyl]-platinum complex with chlorine at 25° for periods of 1 to 2 weeks does not result in significant halogenolysis of the carbon–metal bond.

Chlorination of azobenzene without metallic catalysts

Reaction (A) was repeated except $PdCl_2$ was absent. The azobenzene products were obtained as an orange solid after column chromatography. Analysis by GLC indicated its composition was azobenzene (16%), 4-chloroazobenzene (71%, also includes a small amount of 2-chloroazobenzene), and 4,4'-dichloroazobenzene (13%). Small amounts of 4-chloroazobenzene and 4,4'-dichloroazobenzene were isolated from the solid, each in 90% pure form, by repeated fractional crystallizations from ethanol. The more soluble component was 4-chloroazobenzene, m.p. 87–97°, lit.[14] m.p. 88–89°. The IR spectrum (KBr) shows major absorptions at 1570, 1475, 1145, 1080, 1005, 840, 820, 766, 706, and 680 cm^{-1}. The less soluble component was 4,4'-dichloroazobenzene, m.p. 169–183°, lit.[14] m.p. 185–187°. Its IR spectrum (KBr) is identical to Sadtler Spectrum No. 35379 for the same compound.

Bromination of azobenzene catalyzed by palladium

Reaction (A) was repeated except bromine was added in place of chlorine gas. Analysis of the reaction mixture by GLC revealed that a complex mixture of products had formed. This is expected for HBr catalyzed bromination[7].

A slurry of 0.64 g (0.77 mmoles) of di-μ-bromobis[2-(phenylazo)phenyl]-dipalladium(II)[11] in 30 ml of dioxane was treated with 0.26 g (1.6 mmoles) of bromine for 2 h at 25°. The mixture was taken to dryness under vacuum, and the benzene soluble portion of the residue was chromatographed on alumina. Elution with 25% pentane in benzene afforded 0.11 g (29%) of 2-bromoazobenzene as an orange oil. The major absorptions in its IR spectrum (neat) are at 3030, 1580, 1450, 1150, 1045, 1025, 770, 757, 712, and 684 cm^{-1}.

Isolation of the chloro[2-(phenylazo)phenyl]palladium(II) dimers

As Heck had previously noted[15], complexes of this type are poorly soluble and difficult to purify. Satisfactory elemental analyses were obtained on the red-brown

crystals which formed when their hot acetone solutions were slowly concentrated.

Di-μ-chlorobis[2-(*phenylazo*)*phenyl*]*dipalladium*(*II*) (*I*). The red solid that formed upon heating solutions of azobenzene and $PdCl_2$, as in the initial stages of reaction (A), was collected by filtration. Recrystallization of the solid from acetone afforded (I), m.p. 279–281° dec., lit.[5] m.p. 279–281° dec. (Found: C, 44.7; H, 2.85; Cl, 11.1. $C_{24}H_{18}Cl_2N_4Pd_2$ calcd.: C, 44.68; H, 2.81; Cl, 10.99%.) The far-IR spectrum is reported in Table 1.

Mixture of di-μ-chlorobis[2-(2-*chlorophenylazo*)*phenyl*]*dipalladium*(*II*) (*III*) *and di-μ-chlorobis*[2-(*phenylazo*)-3-*chlorophenyl*]*dipalladium*(*II*) (*IV*). Reaction (A) was terminated after ca. 5 h (the absolute time varies from one reaction to another and depends mostly on the rates of chlorine addition and solution reflux) and cooled to 25°. An orange-red solid (0.35 g, m.p. 302–307° dec.) was collected by filtration and recrystallized from acetone to afford a 4/1 mixture of (III) and (IV), m.p. 281–283° dec. (Found: C, 40.66; H, 2.68. $C_{24}H_{16}Cl_4N_4Pd_2$ calcd.: C, 40.32; H, 2.26%.) The far-IR spectrum is reported in Table 1. Mixtures of (III) and (IV) were also obtained by refluxing dioxane/water solutions of $PdCl_2$ with 2-chloroazobenzene. The relative amounts of (III) and (IV) varied between 4/1 and 1/1, and neither could be isolated in pure form by fractional crystallization.

Di-μ-chlorobis[2-(2-*chlorophenylazo*)-3-*chlorophenyl*]*dipalladium*(*II*) (*V*). A solution of 0.95 g (5.3 mmoles) of $PdCl_2$ and 1.38 g (5.3 mmoles) of 2,2'-dichloroazobenzene in 140 ml of dioxane and 60 ml of water was refluxed for several h and then allowed to stand overnight. Maroon crystals, m.p. 274–275° dec., had formed and were collected by filtration. Recrystallization of the complex from acetone afforded 1.22 g (59%) of (V), m.p. 269–270° dec., lit.[16] m.p. >250°. (Found: C, 37.3; H, 2.4. $C_{24}H_{14}Cl_6N_4Pd_2$ calcd.: C, 36.77; H, 1.80%.) The far-IR spectrum is reported in Table 1.

Reaction of [2-(*phenylazo*)*phenyl*]*palladium*(*II*) *dimers with halogens*

Suspensions of the organopalladium complexes (ca. 0.2 g) in 20 ml of dioxane were treated with an excess of the stoichiometric amount of the halogen at 25°, and the mixture was stirred until a homogeneous solution resulted. The solution was taken to dryness under vacuum, and the benzene soluble portion of the residue was chromatographed on alumina. The azobenzene derived products were eluted with 2% ether in pentane and were analyzed by GLC. The products obtained when (I) and (II) were treated with bromine and chlorine are given in Table 2. Treatment of the mixture of (III) and (IV) with chlorine yielded 2,6-dichloroazobenzene (20%) and 2,2'-dichloroazobenzene (80%) along with a very small amount of azobenzene and 2-chloroazobenzene.

PPh_3 adducts of [2-(*phenylazo*)*phenyl*]*palladium*(*II*) *complexes*

Treatment of acetone suspensions of the organopalladium dimers with in excess of two equivalents of PPh_3 resulted in the formation of homogeneous solutions. After evaporation of acetone, the residues were recrystallized from CH_2Cl_2/pentane mixtures to give 90% yields of the adducts. Complex (I) afforded orange crystals of *trans*-chloro[2-(phenylazo)phenyl]bis(triphenylphosphine)palladium(II) (VI), m.p. 182–185° dec., lit[11] m.p. 190° dec. Its far-IR spectrum (CsI) is identical to the reported spectrum[11]. The mixture of (III) and (IV) yielded a dark purple crystalline mixture of *trans*-chloro[2-(2-chlorophenylazo)phenyl]bis(triphenylphosphine)palladium(II)

(VII) and the 2-(phenylazo)-3-chlorophenyl analogue (VIII), m.p. 224–228° dec. (Found: C, 65.28; H, 4.17. $C_{48}H_{38}Cl_2N_2PdP_2$ calcd.: C, 65.36; H, 4.34%.) The far-IR spectrum (CsI) exhibits a strong absorption at 299 cm^{-1} attributable to ν(Pd–Cl).

Reaction of PPh_3 adducts with HCl

A benzene solution of (VI) was saturated with anhydrous HCl, and after one h the solution was analyzed by GLC. The only component detected, other than solvent, had a retention time identical to that of azobenzene. A benzene solution of the mixture of (VII) and (VIII) was similarly treated and analyzed. The only component detected, other than solvent, had a retention time identical to that of 2-chloroazobenzene.

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