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The Facile Hydrogenation of the Aryldiazonium Functional Group to Hydrazine, Amine, and Ammonia Derivatives

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Aryldiazionium tetrafluoborates react with $Rh(PPh_3)_2Cl(S)$*, and* $[Rh(PPh_3)_2H_2Cl(S)]$ *under hydrogen, (S = solvent, to yield the same arylazorhodium complexes in both cases, and also hydrazine, amine, and ammonia derivatives in the latter . A discussion of the activation of the N≡N triple bond of the aryldiazonium cation is presented.*

Introduction

In recent years there is considerable interest in ammine and ammonia formation in molecular nitrogen fixation reactions.[1,2] These seem to proceed *via* insertion of molecular nitrogen into a M-Ar bond, with formation of an intermediate arylazometal complex, followed by reductive cleavage in the presence of suitable reducing agents.[3] Many arylazometal complexes have been prepared by reacting diazonium cations with transition metal complexes is low oxidation states.[4-12] In none of them the nitrogen function has been hydrogenated without using an additional catalyst. Arylazoplatinum complexes have been hydrogenated only in presence of a heterogeneous catalyst to yield hydrazine, amine, and ammonia derivatives.[13] The aryldiazonium cations can be considered as models of activated molecular nitrogen. Some arylazo complexes can be considered as models of the reduction of molecular nitrogen to ammonia occurring in nitrogen fixing bacteria.[13] All this explains the recent strong interest in the chemistry of these complexes.

In a preliminary note it was reported that aryldiazonium cations are easily hydrogenated in the presence of $Rh(PPh_3)_2H_2Cl(S)$ to yield hydrazine derivatives, without the necessity of using an additional catalyst.[14] This paper gives a full account of a more detailed study of these systems, from the isolation of some intermediates to the complete hydrogenation to amine and ammonia under mild conditions.

Experimental Section

All solvents were of reagent grade quality and were dried, deaired and satured with the suitable gas before use. All the reactions were carried out in an atmosphere of the speciefied pure gas by standard vacuum line techniques.

Infrared spectra were measured using a Perkin-Elmer 337 and Beckman 11 spectrometers. N.m.r. spectra were determined on a Jeol C 60 HL spectrometer using TMS as an internal reference. Mass spectra were determined using a Ithachi-Perkin-Elmer spectrometer. Conductivity was measured with a LKA 3216 B bridge at 25°C.

Aryldiazonium tetrafluoborates were allowed to react with $Rh(PPh_3)Cl$ and $Rh(PPh_3)_2H_2Cl(S)$ under hydrogen[15] in

A) *Chloroform-Methanol medium.* In a typical experiment the dihydride was formed by shaking 1 mmole of $Rh(PPh_3)_3Cl$ in 10-15 ml of $CHCl_3$ in a pressure bottle under hydrogen (1-3 atm) till a yellowish solution formed.[15] This immediately turned dark green upon addition of a stoicheiometric amount of the diazonium salt $p\text{-}XC_6H_4N_2BF_4$ (X = H, CH_3, F) dissolved in 8-9 ml of MeOH, at 0°C, and then red-brown within 15-20′. Orange microcrystals of the arylhydrazine complex (I) precipitated out within 1-4 hours, at r.t.. After filtration, the precipitate was washed with $CHCl_3$, MeOH and ether, and dried in vacuo, yield 150 mg. To the solution, ether was added dropwise till a yellow product precipitated out. This did not contain nitrogen and was not further investigated. The reaction with $p\text{-}FC_6H_4N_2BF_4$ also gave $p\text{-}FC_6H_4NHNH_3Cl$, which was isolated by adding ether dropwise very slowly in order to prevent the coprecipitation of the yellow product. It was identified by comparing its i.r. spectrum to that of an authentycal sample[16], and by its elemental analysis.

Greene microcrystals were obtained by using a

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smaller amount of $CHCl_3$ (8-9 ml) and cooling the green solution at −78°C, yield 150-200 mg. An additional amount of green product was obtained by bubbling hydrogen very vigorously through the solution for 15-20′, total yield 250-300 mg. The same green compounds were obtained from $Rh(PPh_3)_3Cl$ in $CHCl_3$ and $p\text{-}XC_6H_4N_2BF_4$ (X = H, F) in MeOH under nitrogen, better in the dark. All of them slowly dissolve in $CHCl_3$ under hydrogen (3-4 atm) in a pressure bottle giving a reddish solution from which orange microcrystals of (I) precipitated out. (I) is soluble in pyridine and insoluble in the most common organic solvents. They decompose at 230-250°C.

B) Benzene-Methanol medium. The dihydride was formed by bubbling hydrogen very vigorously through 40 ml of benzene with 1 mmole of $Rh(PPh_3)_3Cl$ until the volume was reduced to *ca.* 10 ml. 1 mmole of diazonium salt in 8 ml of MeOH was added at *ca.* 5°C, with stirring. At this point, different products were obtained following different paths 1), 2), 3).

1) Hydrogen was bubbled very vigorously for 15-20′ further reducing the volume to 7-8 ml. A green powder precipitated. The hydrogen flow was continued at a lower rate 1 hour. The suspension was filtered and the precipitate was washed with benzene, methanol, yield 150-200 mg. (Continuing the hydrogen flow for longer some $Rh(PPh_3)_2H_2Cl\cdot C_6H_6$ coprecipitated).

2) The solution turned dark red-brown in 15-20′ at r.t., while hydrogen was gently bubbled. By bubbling dry HCl after two hours, the solution turned orange, and $p\text{-}XC_6H_4NHNH_3Cl$ precipitated within few minutes (X = H, F, CH_3), yield 50%. These products were identified by comparing their i.r. spectra to those of authentic samples.

3) Once the red-brown solution was obtained with $p\text{-}CH_3OC_6H_4N_2BF_4$ (Sec 2), 1 mmole more of diazonium salt in 8 ml of MeOH was added, continuing the hydrogen bubbling. The solution turned immediately dark green-brown, and then dark red-brown within 15-20′. Then 1 mmole more of diazonium salt in 8 ml of MeOH was added. The solution pratically did not change color. A tar was obtained by stripping out the solvent. Benzene was added and the system was heated to b.p.. In a few minutes a white precipitate formed. Pale yellow crystals were obtained from CH_2Cl_2–C_6H_6, yield 300mg. This product was identified as $[Rh(PPh_3)_2(NH_2NHC_6H_4OCH_3)_2]BF_4$ by its elemental analysis, i.r. and n.m.r. spectra, and conductivity.

Some NH_4BF_4 and $p\text{-}CH_3OC_6H_4NH_3BF_4$ formed together with $[Rh(PPh_3)_2(NH_2NHC_6H_4OCH_3)_2]BF_4$. When hydrogen was bubbled for 1 day, 80 mg of NH_4BF_4 was recovered. This was identified by its i.r. spectrum, elemental analysis, and with Nessler's reactive.

All the green compounds are insoluble in the most common organic solvents; they decompose in pyridine giving red solutions. They turn red with nitrogen evolution on the exposure to sunlight in some days.

Results and Discussion

Other authors have reported that although $Rh(PPh_3)_3Cl$ reacts easily with aryldiazonium salts no stable products could be isolated.[17] In this laboratory, it was isolated the same green complex by using concentrate solutions of an aryldiazonium tetrafluoborate in methanol and $Rh(PPh_3)_3Cl$ or $Rh(PPh_3)_2H_2Cl(CHCl_3)$ in $CHCl_3$ under nitrogen or hydrogen atmosphere, respectively, in equimolecular quantities, better in the dark, at 0– −78° C. The i.r. spectra of the green products show no bands in the ν(N-H) region, the absence of the BF_4^- anion, several bands in the 1600 cm^{-1} region, a band at 343-341 cm^{-1} (ν(Rh-Cl), and a strong band at 1965 cm^{-1}. They are light sensitive turning red with lost of nitrogen. The i.r. spectrum of the red powder shows only a doublet centered at 1570 cm^{-1} and the band at 1965 cm^{-1}. Thus the other absorptions at *ca.* 1600 cm^{-1} may be due to a N=N double bond. In $Pt(PEt_3)_2(N_2Ar)Cl$ ν(N=N) occurs at *ca.* 1450 cm^{-1}.[12] The band at 1965 cm^{-1} is absent when $CDCl_3$–$MeOD$ is used. The mass spectrum of the cromatographated volatile fraction of the red solution obtained dissolving the green compounds in pyridine was identical to that of pure $CHCl_3$. The band at 1965 cm^{-1} might be due to coordinate chloroform, rather than ν(Rh-H). In fact it is present in the i.r. spectrum of the crystals obtained by bubbling hydrogen very slowly for some days through a $CHCl_3$-MeOH solution of $Rh(PPh_3)_3Cl$,[18] and it is absent in the green complexes obtained using benzene instead of chloroform, even under hydrogen atmosphere. The rest of the i.r. spectrum is practically the same in these two groups of green compounds. The first analyses as $Rh(PPh_3)_2(N_2C_6H_4X)Cl_2\cdot 1/2C_6H_6$ (X = H, F); the latter might have a similar formulation with chloroform as solvate, although several elemental analyses gave chlorine values 1-2% in difect. However $Rh(PPh_3)_2(N_2C_6H_4F)Cl_2\cdot 1/2CHCl_3$ obtained from $Rh(PPh_3)_2HCl_2$ and $p\text{-}FC_6H_4N_2BF_4$ in $CHCl_3$–Et_2O [17], is orange yellow, and its i.r. spectrum does not show the band at 1965 cm^{-1} Many hydrido-complexes of Rh(III) with tertiary phoshines show ν(Rh-H) in the 1960-1980 cm^{-1} region. When $CHCl_3$–MeOH is used under nitrogen atmosphere, it is possible the formation of a Rh-H bond because HCl can be easily cxtracted from the solvent.[20,21] However this possibility has to be excluded by the fact that in the green complexes the band at 1965 cm^{-1} is absent when $CDCl_3$–MeOD was used, even under hydrogen atmosphere, and no H-D exchange has been observed with similar systems.[15]

An orange microcrystalline complex precipitates out by using less concentrated solutions of $Rh(PPh_3)_2H_2Cl$ and $p\text{-}XC_6H_4N_2BF_4$ in $CHCl_3$-MeOH, under hydrogen atmosphere. Elemental analyses indicate their molecular formulae to be $C_{24}H_{22}Cl_3N_2PRhX$ (X = H, F, CH_3). Their i.r. spectra show bands assignable as ν(N-H) at *ca.* 3230 and 3150 cm^{-1}, the absence of the BF_4^{-1} anion and several bands in the 350-

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[18] The i.r. spectrum of this complex shows also the two bands centered at *ca.* 2050 cm^{-1}, due to ν(Rh-H).[15]

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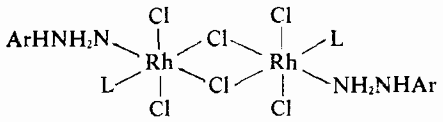
[21] $ArNHNH_2\cdot HCl$ precipitates from $2CHCl_3$-MeOH solution of $Rh(PPh_3)_3Cl$ and $ArNHNH_2$.

Table I. Analytical Data.

Complex	C%		H%		Cl%		N%		P%		Others %	
	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.	Found.	Calcd.
$Rh(PPh_3)_2(N_2C_6H_5)Cl_2 . 1/2C_6H_6$	64.03	64.15	4.74	4.55	8.33	8.42	3.14	3.33	7.22	7.35		
$Rh(PPh_3)_2(N_2C_6H_4F)Cl_2 . 1/2C_6H_6$	63.06	62.81	4.54	4.33	8.46	8.24	3.40	3.26	7.57	7.20	2.19	2.21(F)
$Rh(PPh_3)_2(N_2C_6H_5)Cl_2 . 1/2CHCl_3$	59.37	59.14	4.23	4.15	13.05	14.37	3.24	3.25	7.25	7.18		
$Rh(PPh_3)_2(N_2C_6H_4F)Cl_2 . 1/2CHCl_3$	58.07	57.93	4.09	3.95	12.94	14.08	2.96	3.18	7.25	7.18		
$[Rh(PPh_3)(NH_2NHC_6H_5)Cl_3]_2$	49.40	49.71	4.20	4.01	17.90	18.29	5.03	4.82	5.43	5.23		
$[Rh(PPh_3)(NH_2NHC_6H_4F)Cl_3]_2$	47.59	48.19	3.81	3.73	17.74	17.79	4.72	4.69	5.40	5.23		
$[Rh(PPh_3)(NH_2NHC_6H_4CH_3)Cl_3]_2$	50.21	50.62	4.50	4.24	18.00	17.90	4.70	4.72	5.40	5.21		
$[Rh(PPh_3)_2(NH_2NHC_6H_4OCH_3)_2]BF_4$	60.60	60.56	5.29	5.09	none		6.09	5.65	6.15	6.24	10.55	10.38(Rh)

200 cm^{-1} region which may be attributed to Rh-Cl stretches. The reaction with p-$FC_6H_4N_2BF_4$ also gave p-$FC_6H_4NHNH_2 \cdot HCl$. On the basis of these results(I) is suggested as a possible structure for the orange products.[13]



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The formation of these products might suggest that HCl intervenes as a necessary source of hydrogen. Tre reaction of the dihydrido-complex and the diazonium salt in benzene-methanol medium produces p-$XC_6H_4NHNH_2 \cdot HCl$ upon introduction of dry HCl. However arylhydrazine has been found in the ethereal extracted from the brownish residue obtained by stripping out the solvent before introducing the acid. Therefore it seems that the HCl role is of neutralising the arylhydrazine once formed.

The green complexes are intermediates in the formation of (I), because this forms when they are shaken with $CHCl_3$ in a pressure bottle under hydrogen (1-3 atm). Arylhydrazine complexes of Rh(III) were prepared directly from, for example, phenylhydrazine hydrochloride and $Rh(PEt_3)_3Cl_3$,[22] while $Pt(PEt_3)_2(N_2C_6H_4X)Cl$ is hydrogenated to $Pt(PEt_3)_2(NH_2NHC_6H_4X)Cl$ only in the presence of an additional heterogeneous catalyst.[12]

NH_4BF_4, p-$CH_3OC_6H_4NH_3BF_4$ and crystals of a cationic complex were isolated when an excess of p-$CH_3OC_6H_4N_2BF_4$ was allowed to react with $Rh(PPh_3)_2H_2Cl . C_6H_6$ under hydrogen atmosphere (see experimental section). The n.m.r. spectrum of the crystals in acetone-d_6 shows peaks at 1.52, 2.20, 2.65, 3.16, and 6.32, with relative intensities of 1, 18.7, 2, 4.7, and 3.3. The two broad peaks at 1.52 and 2.65 disappear upon addition of a small amount of CD_3COOD. Hence these two peaks are probably assignable to protons on two different nitrogen atoms. The i.r. spectrum shows two bands in the ν(N–H) region, and the presence of the BF_4^- group. On the basis of these data and its elemental analysis the complex is likely to be $[Rh(PPh_3)_2(NH_2NHC_6H_4OCH_3)_2]BF_4$.

When the green complexes form from $Rh(PPh_3)_2H_2Cl(S)$ two mechanisms are the most likely:

1) direct hydrogen displacement

$$L_nRhClH_2 + ArN_2^+ \rightleftharpoons L_nRhCl(N_2Ar)^+ + H_2$$

as it happens in

$$Co(PPh_3)_3H_3 + N_2 \rightleftharpoons Co(PPh_3)_3HN_2 + H_2 \; ^{23}$$

2) insertion of the diazonium cation into a Rh–H bond

$$L_nRhClH_2 + ArN_2^+ \rightleftharpoons L_nRhCl(NH{=}NAr)H^+$$

with partial reduction of the diazonium group, and formation of a metal di-imide, e.g. $Pt(NH{=}NAr)(PEt_3)_2Cl^+$ from $Pt(PEt_3)_2HCl$[13] or $Ir(NH{=}NAr)(PPh_3)_3H_2^+$ from $Ir(PPh_3)_3H_3$[1,4] followed hydrogen elimination

$$L_nRhCl(NH{=}NAr)H^+ \rightleftharpoons L_nRhCl(N_2Ar)^+ + H_2$$

The action of an alcohol on tertiary phosphine complexes of transition metal halides produces hydrido-complexes and the corresponding aldehyde.[24] When the green complexes form from $Rh(PPh_3)_3Cl$ and the diazonium salt from benzene-methanol medium under nitrogen, no formaldehyde is produced. Therefore in this case, mechanism 1) and 2) are excluded. Their i.r. spectra do not show any band for N≡N triple bond. Therefore it seems that the bond-order lowering of the diazonium salt can happen by direct electron transfer from the metal to the nitrogen function, without being necessary its insertion into a M–H bond as in 2). In $Pt(PEt_3)_2(N_2Ar)Cl$ and $Pt(PEt_3)_2(HN{=}NAr)ClBF_4$ the hydrogenation to $Pt(PEt_3)_2HCl$, amine and ammonia occurs only in the presence of a heterogeneous catalyst under drastic conditions. $Pt(PPh_3)_3(N_2Ar)^+BF_4$ reacts with hydrogen yielding $[Pt(PPh_3)_3H]BF_4$, ArH and N_2, without formation of any compounds having N–H bonds. $Ru(N_2Ar)_2(PPh_3)_2Cl$ BF_4 is reduced to NH_3 and $ArNH_2$ with sodium amalgam. It is noticeable that with the systems here described ammonia and amine are produced under mild conditions.

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