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A Novel Arylazoplatinum Complex which is Readily Hydrogenated

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A novel arylazoplatinum complex has been prepared by displacement of diphenylacetylene from diphenylacetylenebis(triphenylphosphine)platinum using an aryldiazonium salt. If the reaction is performed under hydrogen, followed by addition of dry hydrogen chloride, an arylhydrazonium salt can be isolated, thus a facile homogeneous hydrogenation of an arylazoplatinum complex has been achieved for the first time.

I.r., n.m.r. and conductivity data support the formulae given and it is reasonable to speculate that the intermediate reactive in hydrogenation is a platinum(II) species with a readily available coordination site.

Introduction

Recent studies on the reduction of coordinated dinitrogen have confirmed the role of transition metal ions in biological nitrogen fixation,[1] and stimulated speculation that arylazo transition metal complexes might be considered as model systems for nitrogenase.[2] This and the fact that the arylazogroup is isoelectronic with nitric oxide, has recently aroused great interest in the chemistry of arylazo complexes and their relationship to the mode of co-ordination of analogous nitrosyl systems.[3]

Most of such arylazo complexes have been synthesized directly by reacting metal complexes which contain the metal as a hydride complex or in the zero or low oxidation state, with diazonium salts $ArN_2^+ BF_4^-$,[4] or, recently, with 1,3-diaryltriazenes, ArHN–N=NAr or 1-methyl-1,3-diaryltriazenes, Ar(Me)N–N=NAr,[5] which are known to cleave readily in acid solution forming the corresponding amines and diazonium cations.[6]

Generally they decompose according to the reaction

$$M{-}N{=}NAr \xrightarrow[\Delta]{h\nu} M{-}Ar + N_2$$

which reverses the molecular nitrogen insertion into a M–C σ-bond postulated by Volpin *et al.* as the key step in the simultaneous formation of ammonia and amine.[7] Of more interest is the hydrogenation of the arylazo functional group,[2] although in the natural systems molecular hydrogen is an inhibitor of nitrogen fixation.[1] Till now, only Rh^I and Rh^{III} complexes have been shown to promote the easy hydrogenation of the diazonium group to hydrazine and, in one case, ammonia derivatives in high yield, under mild conditions.[5,8–10] The arylazo platinum and related aryldi-imine complexes reported can not be easily hydrogenated,[2,11] although $[Pt(PPh_3)_3(N_2Ar)](BF_4)$ and $[Pt(PPh_3)_3(HN{=}NAr)](BF_4)_2$ interact with molecular hydrogen at room conditions, to yield $[Pt(PPh_3)H](BF)_4$, with nitrogen evolution.[11]

We would like to report a novel arylazoplatinum complex which undergoes to facile hydrogenation to arylhydrazine derivatives.

Experimental

$Pt(PPh_3)_2(PhC{\vdots}CPh)$ was prepared according to the literature methods.[12] Diazonium salts were prepared in the usual way.

All solvents were of reagent grade quality and were dried, deaerated and saturated with the suitable gas before use.

Infrared spectra (nujol mull) were recorded on a Perkin–Elmer 457 instrument from 4000 to 250 cm^{-1} and were calibrated with polystyrene. ^1H n.m.r. spectra were measured in acetone-d_6 or $CDCl_3$ on a Jeol C 60 HL instrument, with TMS as internal standard. Electronic spectra were taken on a Unicam SP 800 spectrophotometer. The g.l.c. analysis was made on a Perkin–Elmer F11 gas cromatography. Conductivity was measured on a Philips conductivity bridge PR9500.

(Phenylazo)bis(triphenylphosphine)platinum(II) (tetrafluoborate) (I)

To a benzene solution of $Pt(PPh_3)_2(PhC\vdots CPh)$ (15 ml, 1 mmol) an equimolecular amount of $C_6H_5N_2^+ BF_4^-$ suspended in 12 ml of EtOH was added under nitrogen, with stirring in the dark at 10–15°C. Reducing the volume of the formed red solution to *ca.* 10 ml by a vigorous nitrogen flux the brick–orange microcrystalline product precipitated. This was collected on a filter, washed with EtOH and Et_2O and dried under vacuum (60%). Adding *ca.* 100 mg of $NaBH_4$ dissolved in 10 ml of EtOH to the remaining solution, the starting complex was recovered (30% of the initial amount).

Analogously prepared were (*p*-tolylazo)bis(triphenylphosphine)platinum(II)(tetrafluoborate) and (*p*-fluorophenylazo)bis(triphenylphosphine)platinum(II) (tetrafluoborate) as brick–orange microcrystalline complexes.

They are slightly soluble in MeOH, EtOH and soluble in acetone, CH_2Cl_2 and $CHCl_3$ with decomposition.

Hydrogenation of (I)

Performing the above preparative reaction under a hydrogen atmosphere (room condition) the initial red solution turns orange in a few hours. After *ca.* 10 hr, upon introduction of dry HCl, $p\text{-}RC_6H_4NHNH_2 \cdot HCl$ (identified by elemental analysis and i.r.) precipitates in a few minutes (40–50% yield). The platinum complex was recovered from the remaining solution as *cis*-$Pt(PPh_3)_2Cl_2$ (identified by m.p. and i.r.). No formation of platinum metal was observed.

Reaction of (I) with I^-, N_3^-, Cl^-

An excess of NaI or NaN_3 was added to a MeOH suspension of (I) (0.2 mmol, 5 ml). After a few hours $Pt(PPh_3)(N_2Ar)X$ (X = I, N_3) was filtered off and identified by elemental analysis and by comparison with samples obtained from $[Pt(PPh_3)_3(N_2Ar)]BF_4$ as reported in ref. 11). By using LiCl or HCl, pure *cis*-$Pt(PPh_3)_2Cl_2$ (identified by m.p. and i.r.) formed.

With the same experimental conditions by using NaI and an excess of HBF_4 (water solution, 48%), $[Pt(PPh_3)_2(I)(NH{=}NC_6H_4F\text{-}p)](BF_4)$ precipitated as yellow crystals identical to that reported in ref. 11.

Upon treatment with NEt_3, this complex yields $Pt(PPh_3)(N{=}NC_6H_4F\text{-}p)$ which reverts to the starting material with HBF_4.

Reaction of (I) with Carbon Monoxide or PhC⋮CPh

(I) suspended in EtOH (0.300 mg, 5 ml) is recovered unreacted on bubbling CO for 10 hr, at room conditions. Upon adding $NaBH_4$ dissolved in EtOH (100 mg, 5 ml), gas evolution occurs and $Pt(PPh_3)_2(CO)_2$ (identified by elemental analysis and i.r.) precipitates.

With the same experimental conditions, but under an inert atmosphere upon addition of $NaBH_4$ and an excess of PhC⋮CPh, $Pt(PPh_3)_2(PhC\vdots CPh)$ precipitates (identified by i.r.).

In the solvent, the presence of the corresponding hydrocarbon was detected by g.l.c. analysis.

Results and Discussion

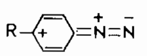
Cenini *et al.*[11] reported that $Pt(PPh_3)_2L$ ($L = CH_2{:}CH_2$, $CH_2{:}CH \cdot C\vdots N$) reacts with diazonium salts yielding unidentified products having a lower content of nitrogen with respect to the simple oxidative addition compound $[Pt(PPh_3)_2L(N_2Ar)](BF_4)$ expected.

We have found that (diphenylacetylene)bis(triphenylphosphine)platinum, $Pt(PPh_3)_2(PhC\vdots CPh)$, reacts with diazonium salts, $(p\text{-}RC_6H_4N_2)(BF_4)$($R = H$, CH_3, F), in a benzene–ethanol medium at r.t., under nitrogen in the absence of light, to form brick–orange microcrystalline complexes whose elemental analysis corresponds to an empirical formula $Pt(BF_4)(N_2Ar)(PPh_3)_2$ (I).

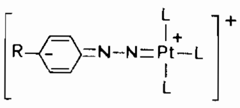
The i.r. of (I) shows a band of weak or medium intensity only for R = CH_3, F, pratically in the same region where the four-co-ordinated complexes $[Pt(PPh_3)_3(N_2Ar)](BF_4)$ (II) or $Pt(PPh_3)_2(N_2Ar)X$ (III) present a band which was tentatively assigned to $\nu(N{=}N)$.[11]

The n.m.r. spectrum shows a complex resonance for the azo-moiety centered at *ca.* τ 3.6, in a region where quinone systems usually absorb.[13] This value is close, though somewhat lower, to those reported for (II) and (III), and is shifted to higher field than that of the corresponding diazonium cations ($\Delta\tau$ *ca.* 2).

The electronic spectrum shows a strong absorption due to co-ordinated PPh_3 and a broad shoulder of weak intensity at lower energy, for which we estimated a maximum at *ca.* 470 nm, in a region where the $n \rightarrow \pi$ absorption of the azo-linkage of (II) (420 nm) and (III) (500 nm) occurs. On the basis of the spectroscopic data found and because for (II) and the corresponding aryldi-imine complexes $[Pt(PPh_3)_2(HN{=}NC_6H_4R\text{-}p)](BF_4)_2$ the energy of the $n \rightarrow \pi$ absorption increases on increasing the value of the Hammett's constant σ_H of the R groups, Cenini *et al.* suggested that the conjugation of the π-electron system of the metal is not involved and that the azo-linkage is stabilized by resonance formula such as (A) in the formation of the bond with platinum:



(A)



(B)

In complex (I) probably the same is true. This is the opposite of Parshall's results for the $Pt(PEt_3)_2(N{=}NC_6H_4R\text{-}p)X$ series for which resonance formula such as (B) participates in the stabilization of the complex, confirming that the basicity of the phosphine and the presence of charge greatly influence the electronic distribution on the azo-group.[2,11,14]

The i.r. spectrum of (I) shows also a broad band at 1100–1000 cm^{-1} for the BF_4^- group sugesting that this is not fully co-ordinated through a fluorine atom.[15] In solution of polar solvents (I) behaves as an electrolyte with unusually high value of conductivity for a singly charged cationic complex. This suggests the presence of the equilibria

$$Pt(PPh_3)_2(N_2Ar)(FBF_3) \overset{a}{\rightleftharpoons} [Pt(PPh_3)_2(N_2Ar)(Solvent)]^+ + BF_4^- \overset{b}{\rightleftharpoons} [Pt(PPh_3)_2(N_2Ar)]_2^{2+} + 2\,BF_4^-$$

In order to explain the low value of conductivity (*ca.* 16–17 ohm^{-1} cm^2 mol^{-1} for *ca.* $10^{-3}M$ solutions in nitrobenzene) of $M(BF_4)Cl(CO)(HN{=}NAr)(PPh_3)_2$ (M = Ru, Os), Robinson *et al.* proposed the solvent dependent equilibrium similar to (a).[5] Equilibrium (b), involving a dimeric doubly charged cationic complex, would account for the high value of Λ found for (I) (see Table). These equilibria involve four-co-ordinated species because a three-co-ordinated complex of Pt(II) is unlikely. In solid, it is likely that *i*) either the BF_4^- group is weakly co-ordinated, with a long distance for the Pt–F bond as found in $Cu(en)_2(BF_4)_2$[16] or *ii*) is dimeric, with a structure similar to that of $[Pt(PPh_3)_2(N_2H)]_2(BPh_4)_2$ which is known to have the structure drawn in Figure 1, with Ar = H.[17] The resonance formula (A)-would favor such a structure, because of the presence of the two electron lone pairs on the terminal nitrogen atom.

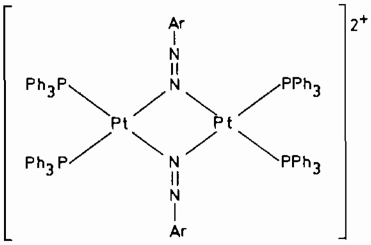
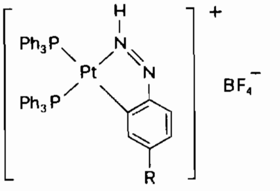


Figure 1. Proposed dimeric structure for the cation of $Pt(BF_4)(N_2Ar)(PPh_3)_2$ (I).

The possibility that (I) is actually a four co-ordinated complex of the type



derived from the simultaneous formation of a metal–carbon σ-bond and proton transfer to the azo-function as observed in the reaction of Vaska's compound with ArN_2BF_4 reported by Sutton *et al.*,[18] has to be discarded because no evidence of such a proton was found in the i.r. and n.m.r. spectra of (I).

The formation of (I) can be visualized as replacement of diphenylacetylene in the coordination sphere of platinum by the arylazo-ligand, probably *via* a cationic acetylene platinum(II) complex, $[Pt(PPh_3)_2(PhC{:}CPh)(N_2Ar)](BF_4)$ (IV). Complexes of this type, with a methyl group instead of the arylazo one, have been recently synthesized and extensively studied by Clark and co-workers.[19]

Some of the chemistry of (I) is summarized in Figure 2. It reacts with NaN_3, NaI, LiCl, HCl, $CHCl_3$ in a similar way as (II). With NaI and HBF_4 in EtOH, it yields $[Pt(PPh_3)_2(HN{=}NAr)I]BF_4$, which reverts to (II) upon treatment with NEt_3. With carbon monoxide in EtOH suspension it is recovered unreacted at r.t. also after several hours, but in the presence of $NaBH_4$ nitrogen evolution promptly occurs and $Pt(PPh_3)_2(CO)_2$[20] precipitates; under an inert atmosphere, upon

TABLE. Analytical and Spectroscopic Data for (I).[a]

Ar	C	H	N	Λ_M	$\nu_{-N=N-}$	$\tau_{C_6H_4}$
C_6H_5	55.20 (54.95)	3.86 (4.01)	3.066 (3.12)	28.1	–	not detected
$p\text{-}CH_3C_6H_4$	55.66 (54.90)	4.02 (4.19)	3.019 (3.13)	27.5	1595	3.6[b]
$p\text{-}FC_6H_4$	54.13 (54.55)	3.68 (3.77)	3.006 (2.95)	27.2	1600	3.5[b]

[a] Found values in parentheses. Conductivity for *ca.* $10^{-3}M$ solutions in nitrobenzene at 25° C.

[b] Two broad and complexes doublets centered at this value.

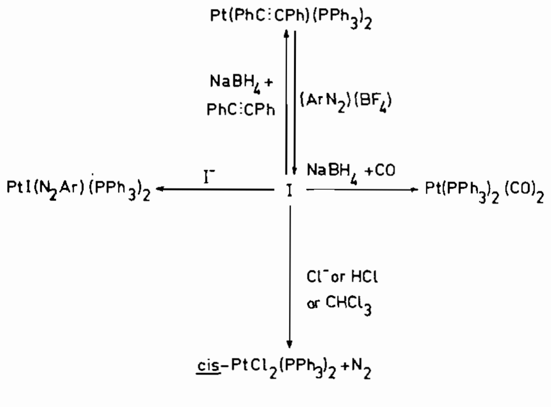


Figure 2. Reactions of $Pt(BF_4)(N_2Ar)(PPh_3)_2$ (I).

addition of PhC:CPh, $Pt(PPh_3)_2(PhC{:}CPh)$ crystallizes out. Probably these two last reactions occur *via* the $Pt(PPh_3)_2$ reactive intermediate,[21] following the scheme

$$\text{(I)} \xrightarrow{\text{NaBH}_4} \text{N}_2 + \text{Ar H} + \text{Pt(PPh}_3)_2 \xrightarrow{\text{L}} \text{Pt(PPh}_3)_2\text{L (L = 2CO, PhC:CPh).}$$

No formation of N–H bonds was noted, the organic group being transformed into the corresponding hydrocarbon with nitrogen evolution.

Of greater interest are the results of the hydrogenation of (I). Performing the preparative reaction of (I) in a hydrogen atmosphere (room conditions) an initial red solution is obtained (as under a nitrogen atmosphere) but further reaction occurs and addition of dry HCl, after a few hours, results in precipitation af arylhydrazonium chloride (R = H, CH_3, F).* It should be noted that (I) reacts with hydrogen chloride alone in a totally different way (see Figure 2). No formation of colloidal platinum could be noted. Thus the facile homogeneous hydrogenation of an arylazoplatinum complex has been achieved for the first time. It is reasonable to speculate that the intermediate reactive in hydrogenation is a platinum(II) species of the type (IV) or one of those involved in equilibria a) and b) with a readily available coordination site on displacement of the weakly bound acetylene or solvent or BF_4^- group. This is one of the criteria important in the activity of Wilkinson's catalyst,[22] which also promotes the facile hydrogenation of aryldiazonium salts.[5,8–10] This coordination site would activate a hydrogen molecule transferring it to the azo-function. The lack of availability of such a readily coordination site in Parshall's complexes would prevent the facile hydrogenation of the azo-moiety, even if the N=N linkage results more activated than in (I), having a weaker double bond character (see formulae (A) and (B)). The fact that complex (II) does not yield any compound with N–H bonds, even though it interacts with molecular hydrogen to give $[Pt(PPh_3)_3H](BF_4)$ with nitrogen evolution, might be due to displacement of the azo-group before it can react with hydrogen, comfirming the suggestion that in complex (II) the azo-function is weakly bound to platinum.[11]

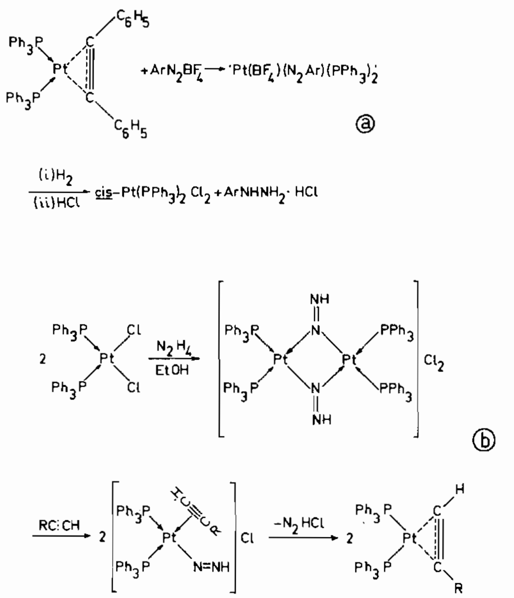


Figure 3. Proposed mechanisms for the (a) hydrogenation of the aryl-diazonium cation, (b) formation of platinum-acetylene complexes.

It is interesting to note that the formation of (I) and its consecutive hydrogenation substantially reverse the proposed mechanism of formation of many platinum-acetylene complexes (see Figure 3).[23]

Performing the above hydrogenation, using $Pt(PPh_3)_2(PhC{:}CH)$ and without adding HCl, a yellow crystalline compound with an acetylenic and N–H bonds formed. These results will be given in another paper.

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* The platinum complex was recovered as *cis*-$Pt(PPh_3)_2Cl_2$. The fate of the acetylene molecule was not investigated.

** Parshall's arylazo-platinum complexes could be hydrogenated only in the presence of an additional heterogeneous catalyst, as Pt/or Pd/charcoal.

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