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NEW CATIONIC ARYLDIAZO, ARYLDIIMINE AND ARYLHYDRAZINE COMPLEXES OF PLATINUM

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Summary

The preparation of some new cationic aryldiazo complexes of platinum of formula *trans*-$[Pt(N_2Ar)(PEt_3)_2L]^+$, where $N_2Ar = N_2C_6H_4F$-*m* or -*p* and L = NH_3, Py, Et_3P or EtNC, is described. Protonation of these complexes gives the corresponding aryldiimide complexes *trans*-$[Pt(NHNAr)(PEt_3)_2L]^+$, and reduction of the protonated complexes with molecular hydrogen in the presence of a catalyst gives the arylhydrazine complexes *trans*-$[Pt(NH_2NHAr)(PEt_3)_2L]^+$. Some of the spectroscopic properties of these new complexes are reported and discussed.

Introduction

There is considerable current interest in the preparation and properties of transition metal complexes containing the aryldiazo ligand [1,2]. This ligand is electronically very similar to NO, although much less is known about the way in which it bonds to a metal atom. The nitrosyl ligand forms a remarkable variety of metal complexes in some of which it is best regarded as NO^+ and in others as NO^-. However these are only the two extreme bonding situations and many intermediate cases have been recognised [3]. Similarly the aryldiazo ligand can, in principal at least, be present in complexes either as ArN_2^+ or as ArN_2^-. X-ray diffraction studies provide the best way of distinguishing between the various bonding possibilities for the NO ligand, but only a few such studies [4,5] have as yet been carried out on aryldiazo complexes. Spectroscopic evidence can provide some information, and the versatility of ArN_2 as a ligand is illustrated by the fact that values of ν(NN) in the infrared which have been reported [2,6] vary from 1440 to 1882 cm^{-1}.

It seems that a small change in the nature of the other ligands bound to the metal can have a very marked effect on the metal—diazo linkage since, for example, ν(NN) for $[IrCl(N_2Ph)(PPh_3)_3]^+$ and for $[IrCl(N_2Ph)(PPh_3)_2(CNEt)]^+$ differ by over 150 cm^{-1} [2]. However there have been no systematic studies of this effect.

In this paper we report a series of cationic complexes of the type *trans*-$[Pt(N_2Ar)(L)(PEt_3)_2]^+$ (where L is a neutral 2-electron donor ligand) which we have prepared in order to examine the effect of changing L on the metal—diazo linkage. As the aryldiazo ligands we have chosen *p*-$FC_6H_4N_2$ and *m*-$FC_6H_4N_2$, as the ^{19}F NMR data then obtainable can provide information about any changes in the bonding of these ligands to the metal as L is varied.

An additional feature of interest about these cationic complexes is that the related neutral aryldiazo complexes $PtCl(N_2Ar)(PEt_3)_2$ have been proposed as model systems for the biological reduction of dinitrogen [6]. We have therefore briefly examined the reactivity of the cationic aryldiazo complexes for comparative purposes.

In the course of this work we have prepared some new aryldiimide and arylhydrazine complexes which are also described in this paper.

Results and discussion

(a). Preparation

The cationic aryldiazo complexes were prepared from the neutral complex *trans*-$PtCl(N_2Ar)(PEt_3)_2$ [7]. The neutral ligands L were added to an acetonitrile or acetone solution of this complex held at 0° and containing a stoichiometric quantity of either $NaBPh_4$, $NaClO_4$, $NaPF_6$ or $AgPF_6$. Sodium (or silver) chloride is precipitated and after filtration the cationic aryldiazo complexes were readily isolated by evaporation of the solvent and subsequent recrystallisation. In this manner the complexes *trans*-$[Pt(N_2Ar)L(PEt_3)_2]^+$ were prepared, where $N_2Ar = N_2C_6H_4F$-*p* or $N_2C_6H_4F$-*m* and $L = CNC_2H_5$, pyridine (Py), PEt_3, or NH_3 (Table 1). The stereochemistry of these complexes was established as *trans* by the method of Jenkins and Shaw [8]. Thus the ^1H NMR spectra of all the complexes in deuterioacetone solution show 1/4/6/4/1 quintets centred at ca. 8.74 - 8.92 τ with a line separation of 8 Hz, and seven line multiplets at slightly lower field with line separation of 4 Hz.

The complexes were all obtained as brightly coloured purple/red crystals. They are soluble in polar solvents such as acetone or acetonitrile but are insoluble in non-polar solvents such as benzene or hexane.

The attempted preparation of the complexes *trans*-$[Pt(N_2Ar)(CO)(PEt_3)_2]^+$ ($N_2Ar = N_2C_6H_4F$-*p* or $N_2C_6H_4F$-*m*) gave purple/red solid products if the solvent was evaporated rapidly after filtration. However these products always contained significantly less nitrogen than required for the above formulation and, on attempted recrystallisation at room temperature, colourless products were obtained which contained no nitrogen and analysed correctly for *trans*-$[PtAr(CO)(PEt_3)_2]^+$. All the aryldiazo complexes we have prepared are susceptible to this mode of decomposition and indeed arylplatinum, rather than aryldiazo platinum complexes, were obtained in every case if the preparative reactions were carried out at room temperature instead of at 0°. Once formed, however, the complexes could be recrystallised at room temperature without appreciable decomposition. All the cationic complexes do decompose on refluxing in acetone solution however, and qualitatively, as judged by the rate of decomposition, the stability order is $L = NH_3 \simeq Py$, $> PEt_3 \simeq RNC > CO$. In general the complexes with *m*-$FC_6H_4N_2$ as the aryl-

TABLE 1

Compound	Analysis found (calcd.)(%)			IR (cm^{-1})	
	C	H	N	ν(NN)	ν(NH)
trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_3BPh_4$	58.2 (58.2)	7.2 (7.0)	2.8 (2.8)	1581^a	
trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_2(CNEt)]BPh_4$	57.8 (58.2)	6.2 (6.4)	4.6 (4.5)	1580^a	
trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_2(Py)]BPh_4$	59.4 (59.3)	6.3 (6.3)	4.4 (4.4)	1585^a	
trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_2(NH_3)]ClO_4$	32.5 (32.4)	5.9 (5.6)	5.7 (6.4)	1574^a	
trans-$[Pt(N_2C_6H_4F\text{-}m)(PEt_3)_3]BPh_4$	58.5 (58.2)	7.2 (7.0)	2.7 (2.8)	1580^b	
trans-$[Pt(N_2C_6H_4F\text{-}m)(PEt_3)_2(CNEt)]BPh_4$	58.1 (58.2)	6.2 (6.4)	4.5 (4.5)	1579^b	
trans-$[Pt(N_2C_6H_4F\text{-}m)(PEt_3)_2(Py)]BPh_4$	59.1 (59.3)	6.2 (6.3)	4.4 (4.4)	1582^b	
trans-$[Pt(N_2C_6H_4F\text{-}m)(PEt_3)_2(NH_3)]ClO_4$	32.5 (32.4)	5.8 (5.6)	5.8 (6.4)	1582^b	
trans-$[Pt(NHNC_6H_4F\text{-}p)(PEt_3)_2(CNEt)](ClO_4)_2$	31.5 (31.2)	4.8 (5.0)	5.6 (5.2)		3215^a
trans-$[Pt(NHNC_6H_4F\text{-}p)(PEt_3)_2(Py)](ClO_4)_2$	33.6 (33.2)	4.6 (4.8)	4.8 (5.0)		3218^a
trans-$[Pt(NHNC_6H_4F\text{-}p)(PEt_3)_2(NH_3)](ClO_4)_2$	28.0 (28.0)	5.5 (4.9)	5.7 (5.4)		3216^a
trans-$[Pt(NHNC_5H_4F\text{-}m)(PEt_3)_2(CNEt)](ClO_4)_2$	31.6 (31.2)	4.4 (5.0)	5.6 (5.2)		3216^a
trans-$[Pt(NHNC_6H_4F\text{-}m)(PEt_3)_2(Py)](ClO_4)_2$	33.4 (33.2)	4.8 (4.8)	4.9 (5.0)		3218^a
trans-$[Pt(NHNC_6H_4F\text{-}m)(PEt_3)_2(NH_3)](ClO_4)_2$	28.2 (28.0)	5.0 (4.9)	5.1 (5.4)		3218^a
trans-$[Pt(NH_2NHC_6H_4F\text{-}p)(PEt_3)_2(CNEt)](ClO_4)_2$	31.1 (31.1)	5.5 (5.2)	5.5 (5.2)		3230, 1656^a
trans-$[Pt(NH_2NHC_6H_4F\text{-}p)(PEt_3)_2(Py)](ClO_4)_2$	32.6 (33.0)	5.4 (5.0)	4.2 (5.0)		3222, 1654^a
trans-$[Pt(NH_2NHC_6H_4F\text{-}p)(PEt_3)_2(NH_3)](ClO_4)_2$	28.1 (28.0)	5.5 (5.2)	5.5 (5.4)		3230, 1656^a
trans-$[Pt(NH_2NHC_6H_4F\text{-}m)(PEt_3)_2(CNEt)](ClO_4)_2$	31.4 (31.1)	5.5 (5.2)	5.3 (5.2)		3224, 1610^a
trans-$[Pt(NH_2NHC_6H_4F\text{-}m)(PEt_3)_2(Py)](ClO_4)_2$	32.7 (33.0)	5.3 (5.0)	4.8 (5.0)		3222, 1618^a
trans-$[Pt(NH_2NHC_6H_4F\text{-}m)(PEt_3)_2(NH_3)](ClO_4)_2$	28.3 (29.0)	5.4 (5.2)	5.1 (5.4)		3220, 1616^a
trans-$[Pt(C_6H_4F\text{-}p)(PEt_3)_2(CO)]BPh_4$	59.4 (59.2)	5.9 (5.8)			
trans-$[Pt(C_6H_4F\text{-}m)(PEt_3)_2(CO)]BPh_4$	59.1 (59.2)	6.0 (5.8)			

[a] In nujol mulls. [b] In KBr discs.

diazo ligand are more stable with respect to N_2 loss than those with p-$FC_6H_4N_2$. Other workers have shown that in the series of complexes $[Pt(N_2C_6H_4X\text{-}p)(PPh_3)_3]^+$ the stability is also very sensitive to the nature of the *para* substituent X [9].

Recrystallisation of some of the products [e.g. *trans*-$Pt(N_2Ar)(NH_3)(PEt_3)_2$] from ethyl acetate gave a product containing one mole of ethyl acetate of crystallisation per mole of complex, but this was readily removed under vacuum at room temperature.

(b). Reactions

All the aryldiazo platinum complexes we have prepared react readily in methanol solution with acids such as perchloric acid to give bright yellow diimide complexes in almost quantitative yield. These complexes are indefinitely stable in the solid state. However, the reaction in which they are formed is reversible, and freshly prepared solutions of the diimide complexes rapidly assume a red colour on standing. The equilibrium can be driven over in either direction by the addition of base (e.g. Et_3N) or acid to the solutions. The neutral complexes *trans*-$PtCl(N_2Ar)(PEt_3)_2$ may be similarly protonated, and it has been shown by ^1H NMR spectroscopy, using ^{15}N, that the proton is most probably on the nitrogen atom directly bound to platinum [6].

We have been unable to reduce the cationic diazo complexes reported in this paper without at the same time breaking the platinum—diazo linkage. However the dicationic diimine complexes *trans*-$[Pt(NHNAr)L(PEt_3)_2]^{2+}$ may be reduced to the arylhydrazine complexes *trans*-$[Pt(NH_2NHAr)L(PEt_3)_2]^{2+}$ by the action of hydrogen in methanol solution at room temperature in the presence of a platinum catalyst. The monocationic complexes *trans*-$[PtCl(NH_2NHAr)(PEt_3)_2]^+$ are similarly reduced [4], although the complexes *trans*-$[Pt(NHNAr)(PPh_3)_3]^{2+}$ can not be reduced in this way without breaking the platinum—nitrogen bond [9].

(c). Spectroscopic studies

Infrared spectra. The cationic diazo complexes show strong absorptions at ca. 1600 cm^{-1} which are not seen in the spectra of the aryldiimine or arylhydrazine complexes. This absorption is also not present in the aryl complexes *trans*-$[PtAr(L)(PEt_3)_2]^+$ and it is therefore most probably due to ν(N=N). The same assignment of a band at ca. 1600 cm^{-1} present in the IR spectra of the cationic complexes $[Pt(N_2Ar)(PPh_3)_3]^+$, has been made previously [7]. However it is rather surprising that the variation in the position of this band in the cationic complexes we have prepared is only 18 cm^{-1} for the whole range of different ligands L used. In the neutral complex *trans*-$PtCl(N_2Ar)(PEt_3)_2$ ν(N=N) occurs at 1463 cm^{-1} and this assignment has been verified by ^{15}N substitution. It would be expected that ν(N=N) in a cationic complex would be a good deal higher than in a corresponding neutral complex but, in view of the small variation in ν(N=N) and in the absence of confirmatory ^{15}N experiments it is not possible to go any further than this. The diimine complexes as mentioned earlier do not show the ν(N=N) band but they do exhibit a weak absorption at ca. 3200 cm^{-1} which may be assigned to ν(N—H). The arylhydrazine complexes also show this band and, in addition, there is a strong absorption at 1610 - 1656 cm^{-1} which must be due to the presence of the NH_2NHAr ligand. Other NH bands in the 1100 cm^{-1} region, observed previously in the spectra of aryldiimine and arylhydrazine complexes [6,9] are, in the complexes reported here, obscured by the absorption due to the perchlorate anion.

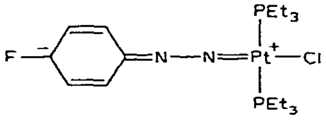
^{19}F NMR spectra. ^{19}F NMR data for the aryldiazo complexes are presented in Table 2. Parshall has previously studied the ^{19}F NMR spectra of the neutral complexes *trans*-$PtCl(N_2Ar)(PEt_3)_2$ ($N_2Ar = N_2C_6H_4F$-*m* or -*p*) and came to the conclusion that the $(Et_3P)_2ClPtN_2$ grouping acts as a strong donor to the benzene ring in the *para*-substituted complex. He suggested that the data could best be accounted for if resonance structures such as (I) make substantial contributions to the electronic character of the platinum complexes [10].

TABLE 2

^{19}F NMR DATA[a]

Compound	δp^b	δm^b	$\sigma_I{}^c$	$\sigma_R{}^c$	$J(^{195}Pt—F)$ (Hz)
trans-$[Pt(N_2C_6H_4F)(PEt_3)_3]BPh_4$	−0.6	−1.6	0.31	−0.03	5.0
trans-$[Pt(N_2C_6H_4F)(PEt_3)_2(CNEt)]BPh_4$	+0.3	−1.1	0.24	−0.04	5.5
trans-$[Pt(N_2C_6H_4F)(PEt_3)_2(Py)]BPh_4$	+0.4	−1.1	0.24	−0.05	6.0
trans-$[Pt(N_2C_6H_4F)(PEt_3)_2(NH_3)]BPh_4$	+1.4	−1.0	0.23	−0.08	6.5
trans-$[Pt(N_2C_6H_4F)(PEt_3)_2(Cl)]$	+2.3	+0.4	0.03	−0.06	5.0

[a] In deuterioacetone solution at 32°. [b] In ppm relative to 5% C_6H_5F as internal standard. [c] Taft σ_I and σ_R parameters [see refs. 10 and 11].



(I)

This suggestion is based on the use of $\delta p - \delta m$ as a measure of the "π-acceptor ability" of the FC_6H_4 ring. However the figure so obtained almost certainly overestimates the importance of resonance as opposed to inductive effects and the method has been shown to give results, when applied to platinum-substituted complexes, which are not necessarily in accord with estimates of "π-acceptor ability" based on other spectroscopic techniques [11,12]. A more realistic interpretation of the data may be made by making use of the Taft σ_I and σ_R parameters [12,13]. A positive value of σ_I (σ_R) indicates that the substituent X in the complex FC_6H_4X withdraws electrons by an inductive (resonance) mechanism with respect to hydrogen. We have calculated these parameters both for the neutral complexes originally prepared by Parshall and for the new cationic complexes reported in this paper (Table 2). It will be seen that the $(Et_3P)_2ClPtN_2$ substituent acts as a π-donor and as a σ-acceptor to the C_6H_4F ring in the neutral complexes, but that neither effect is particularly strong as compared to these effects for other X substituents which have been studied [12,13]. The effect of placing a positive charge on the platinum atom is to make the $L(Et_3P)_2PtN_2$ grouping a better σ-acceptor. However, the positive charge does not affect the π-donor ability of this grouping to nearly the same extent.

Conclusions

The geometry of these platinum diazo complexes is clearly square planar (with two *trans* phosphorus ligands) rather than tetrahedral. They are therefore best regarded formally as Pt^{II} complexes with ArN_2^- rather than as Pt^0 complexes with ArN_2^+. The effect of putting a positive charge on the metal atom is to destabilise the platinum aryldiazo complexes as compared to the corresponding platinum aryl complexes. This destabilisation is most marked for those ligands which are poor σ-donors and good π-acceptors (CO) presumably because such ligands leave the platinum atom with the greatest net positive charge. The ^{19}F NMR data indicates that this positive charge leads to a significantly increased electron withdrawal from the FC_6H_4 ring, and that this takes place largely via a σ-inductive mechanism. Resonance structures such as (I) involving platinum—nitrogen double bonding seem to be relatively unimportant, and this is perhaps not unexpected for the ArN_2^- ligand, which is electronically similar to NO^-. Just as NO^+ is a very good π-acceptor ligand so ArN_2^+ would also be expected to be a good π-acceptor ligand [14]. A study of the ^{19}F NMR spectra of a series of complexes which could be formally regarded as containing the $FC_6H_4N_2^+$ ligand would therefore be of very considerable interest for comparative purposes with the data reported here.

Experimental

The neutral aryldiazo complexes were prepared by published methods [5]. All other chemicals were reagent grade and were used without further purification. All solvents were deaerated with nitrogen before use and all reactions were carried out under nitrogen.

Infrared spectra were recorded using a Perkin—Elmer 257 instrument calibrated against carbon monoxide or polystyrene film. A Varian XL 100 spectrometer was used to record the ^{19}F NMR spectra. Microanalyses were carried out by the microanalytical laboratory of the chemistry department at Cambridge University.

Preparation of complexes

(i). trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_3]BPh_4$ *(or* PF_6*).* The complex *trans*-$[PtCl(N_2C_6H_4F\text{-}p)(PEt_3)_2]$ (500 mg) was stirred with a solution of Et_3P (80 mg) in CH_3CN (20 ml). $NaBPh_4$ (76 mg) was added and stirring was then continued for 1 h. The solution was then filtered, evaporated to dryness, and recrystallised from acetone by addition of ether at 0°. Yield of pale purple crystals: 47%. The PF_6^- salt was similarly prepared by addition of $AgPF_6$ (175 mg) instead of $NaBPh_4$.

(ii). trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_2(Py)]BPh_4$ *(or* ClO_4*).* This complex was prepared as above using pyridine (64 mg) instead of Et_3P. The complex was recrystallised from warm methanol to yield purple crystals (37%). The perchlorate salt was prepared similarly using $NaClO_4 \cdot H_2O$ (96 mg). Yield 25%.

(iii). trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_2(CNEt)]BPh_4$ *(or* ClO_4*).* The complex *trans*-$PtCl(N_2C_6H_4F\text{-}p)(PEt_3)_2$ was stirred in CH_3CN (20 ml) containing EtNC (60 mg). $NaBPh_4$ (260 mg) was added and stirring was continued for 1 h. The solution was then filtered, evaporated to dryness, and excess isocyanide removed under vacuum (0.1 mm/20°). The crude product was washed well with hot water and then recrystallised from warm methanol to give purple crystals. Yield 49%. The perchlorate salt was prepared similarly using $NaClO_4 \cdot H_2O$ (72 mg). Yield 56%.

(iv). trans-$[Pt(N_2C_6H_4F\text{-}p)(PEt_3)_2NH_3]ClO_4$. The complex *trans*-$PtCl(N_2C_6H_4F\text{-}p)(PEt_3)_2$ was stirred with acetone (20 ml) which was saturated with NH_3 by passing a steady stream of this gas through the solution. $NaClO_4 \cdot H_2O$ (72 mg) was then added and stirring was continued for 1 h. The

solution was filtered and evaporated to dryness. The product was recrystallised from methanol by addition of ether at 0° to give violet crystals. It was further recrystallised from ethanol. Yield 82%.

(v). trans-$[Pt(N_2C_6H_4F\text{-}m)(PEt_3)_2L]X$ ($L = PEt_3$, *CNEt, Py,* NH_3; $X = BPh_4$, ClO_4). The complex $PtCl(N_2C_6H_4F\text{-}m)(PEt_3)_2$ was stirred in acetone (20 ml) at 0° containing Et_3P (80 mg), EtNC (60 mg), Py (64 mg) or NH_3(g). $NaBPh_4$ (232 mg) or $NaClO_4 \cdot H_2O$ (96 mg) was added and stirring was continued for 1 h at 0°. The solution was filtered and the filtrate evaporated to leave a crystalline residue. This was recrystallised from warm methanol to yield pale purple crystals. Yield 60 - 70%.

(vi). trans-$[Pt(NHNC_6H_4F\text{-}m$ *or* $\text{-}p)(PEt_3)_2L](ClO_4)_2$ (*L = CNEt, Py or* NH_3). The complexes *trans*-$[Pt(N_2C_6H_4F\text{-}m$ or $\text{-}p)(PEt_3)_2L]ClO_4$ (50 mg) were dissolved in acetone (1 ml). $HClO_4$ (0.1 ml) was added and the solution was stirred before being allowed to stand for 15 min. The salts were crystallised by the addition of ether to give bright yellow crystals. These were washed well with ether and recrystallised from warm methanol containing one drop of $HClO_4$. Yields > 90%.

(vii). trans-$[Pt(NH_2NHC_6H_4F\text{-}m$ *or* $\text{-}p)(PEt_3)_2L](ClO_4)_2$ (*L = CNEt, Py or* NH_3). The complexes *trans*-$[Pt(NHNC_6H_4F\text{-}m$ or $\text{-}p)(PEt_3)_2L](ClO_4)_2$ were dissolved in methanol (10 ml) containing a Pd/carbon catalyst (10%, 5 mg). A slow stream of hydrogen was passed through the solution for 1 h and the Pd/carbon was then filtered off. The volume of the solution was then reduced to 1 - 2 ml and crystallisation was effected by the addition of ether. Yield of pale yellow crystals, 80 - 90%.

(viii). Formation of cationic arylplatinum complexes in reaction with CO. The complexes *trans*-$[PtCl(N_2C_6H_4F\text{-}m$ or $\text{-}p)(PEt_3)_2]$ (250 mg) were dissolved in air free CH_3CN (20 ml) at 0°. CO was passed through the solution and, on addition of $NaBPh_4$ (145 mg), the colour of the solution slowly faded and after 1 h was pale yellow. The solution was filtered, concentrated to a small volume (5 ml), and ether was then added to give white crystals of *trans*-$[Pt(C_6H_4F\text{-}m$ or $\text{-}p)(PEt_3)_2(CO)]BPh_4$. A further crop of crystals was obtained from the solution on standing at — 10°. Yield 80 - 90%.

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