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Aryldiazonium Complexes of Ruthenium Porphyrins

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Introduction

We have recently begun a study of the reactions of aryldiazonium salts with metal macrocycle complexes. In this paper we present our initial results with some porphyrin complexes of ruthenium.

Experimental

All solvents were dried by usual methods and distilled under nitrogen. All reactions were carried out under a nitrogen atmosphere. The complexes [Ru(OEP)(CO)EtOH], (OEP = octaethylporphyrin), and [Ru(TPP)(CO)EtOh] (TPP = tetraphenylporphyrin), were prepared by the literature method [1, 2].

Infrared spectra were recorded on a Perkin Elmer 457 Spectrometer for samples pressed in KBr discs. Visible spectra were recorded using a Cary-17 spectrophotometer. Elemental analyses were carried out at the Centro de Tecnologia do Estado de Minas Gerais (CETEC), Belo Horizonte.

Preparation of [Ru(porphyrin)(N$_2$Ar)L] BF$_4$

In a typical experiment [Ru(TPP)(CO)EtOH] (40 mg, 0.5 mmol) was dissolved in a minimum of dichloromethane and a five-fold excess of aryldiazonium salt added. The solution was heated to reflux until monitoring by visible spectroscopy indicated complete reaction (3–5 h). Upon cooling the unreacted aryldiazonium salt was filtered off and on evaporation of the mother liquor to half volume addition of petroleum ether precipitated the complex. The OEP derivative reacted at room temperature in thirty minutes. The complexes may be recrystallised from acetone–petroleum ether as dark red-brown solids (yields 50–60%).

Results and Discussion

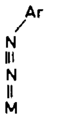
The porphyrin complexes studied were of the type [Ru(porp)(CO)EtOH] (porp = OEP, octaethylporphyrin and TPP = tetraphenylporphyrin). In both cases, reaction with an excess of aryldiazonium ion in dichloromethane, at reflux temperature for TPP and room temperature for OEP, followed by recrystallisation from acetone/petroleum ether gave dark semi-crystalline solids. Some physical properties of the new complexes are given in Table I. The infrared spectrum clearly shows the disappearance of ν(CO) (1940 cm^{-1} for OEP, 1945 cm^{-1} for TPP) and a new broad band at ~1810 cm^{-1} for the TPP derivatives and 1790 cm^{-1} for the OEP complex, along with bands at 1050 cm^{-1} (ν_{asym}(BF$_4$)). Elemental analysis confirmed the products to be [Ru(porp)(N$_2$Ar)L] BF$_4$ due to displacement of CO by the aryldiazenato group. In the case of the $C_6H_5N_2$ and p-$OCH_3C_6H_4N_2$ derivatives of the TPP complex recrystallisation from acetone appears to result in concomitant displacement of the sixth ligand, ethanol.

The limiting coordination geometries for the metal–aryldiazenato linkage in mononuclear complexes are:

Where the group is formally ArN$_2^+$ the aryldiazenato group approximates to the singly-bent structure

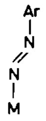
TABLE I. Physical Data for Aryldiazenato–Ruthenium–Porphyrin Complexes.

Complex	Elemental Analysis (Calcd. in parentheses)			ν(NN) cm^{-1}	λ_{max} (log ϵ) nm	
	C	H	N			
[Ru(OEP)(p-NO$_2$C$_6$H$_4$N$_2$)EtOH] BF$_4$	54.9(55.7)	4.3(4.0)	8.9(8.9)	1790	385(5.04)	490(4.88) 525(4.90)
[Ru(TPP)(C$_6$H$_5$N$_2$)acetone] BF$_4$	67.2(66.7)	4.1(4.1)	8.6(8.8)	1810	418(5.09)	518(3.93)
[Ru(TPP)(p-NO$_2$C$_6$H$_4$N$_2$)EtOH] BF$_4$	61.5(62.6)	3.6(3.8)	8.8(9.8)	1815	420(5.26)	515(4.11)
[Ru(TPP)(p-OCH$_3$C$_6$H$_4$N$_2$)acetone] BF$_4$	67.3(65.9)	4.1(4.1)	8.6(8.5)	1810	416(5.12)	518(4.03)



A

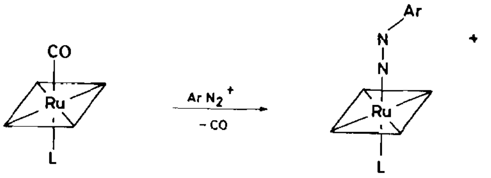
B



C

A or linear B, whereas as ArN_2^- the group adopts the doubly-bent structure C [3].

A number of ruthenium–aryldiazenato complexes have been reported. In *mer*-$[RuCl_3(N_2Ar)(PPh_3)_2]$, $\nu(NN)$ = 1850–1900 cm^{-1}, X-ray crystal structure determinations [4, 5] for Ar = p-$CH_3C_6H_4$ have confirmed the singly-bent nature of the aryldiazenato group. Some bipyridine complexes of type *cis*-$[Ru(bipy)_2(N_2Ar)Cl]^{2+}$ have high $\nu(NN)$ values, 2095 cm^{-1} for Ar = p-$OCH_3C_6H_4$ and 2080 cm^{-1} for p-$CH_3C_6H_4$ in CH_3CN solution and a linear structure is indicated [6]. The high values of $\nu(NN)$ in our complexes indicate a singly-bent structure. They are best formulated as Ru(II)–ArN_2^+ adducts:



It is of interest to note that TPP series shows very little variation in $\nu(NN)$ for differing substituents on the aryl ring, whereas *mer*-$[RuCl_3(N_2Ar)(PPh_3)]$ has $\nu(NN)$ = 1881 cm^{-1}, Ar = Ph; 1884 cm^{-1} for Ar = p-$OCH_3C_6H_4$ and 1858 cm^{-1} for Ar = p-$NO_2C_6H_4$ [5].

To our knowledge this is the first example of an aryldiazenato-metal porphyrin complex formed by direct reaction with aryldiazonium ion. Recently, the X-ray crystal structure of $[Mo(N_2Ph)_2TPP]\cdot C_6H_5NHNH_2$, formed by reaction of $[MoCl_2TPP]$ with excess phenylhydrazine was reported. The aryldiazenato group is doubly bent ($\nu(NN)$ = 1595 cm^{-1}) and the compound is clearly best considered as $[Mo(IV)–PhN_2^-)_2]$.

The aryldiazonium ion is considered to be isoelectronic with the nitrosyl, NO^+, and dinitrogen, N_2, ligands [3]. Both nitrosyl and dinitrogen adducts of ruthenium porphyrins have been prepared. Reaction of NO with [Ru(OEP)(CO)EtOH] and addition of methoxide ion gives [Ru(OEP)(NO)OMe] by displacement of CO while prior photodissociation of [Ru(OEP)(CO)DMF] is necessary for N_2 binding to be observed [9, 10].

The visible spectrum of $[Ru(OEP)(p\text{-}NO_2C_6H_4N_2)EtOH]BF_4$ is shown in Fig. 1. The Soret band is broadened with a slight negative shift and the spectrum is very similar both in appearance and value of extinction coefficients to that of the dinitrogen [9, 10] and nitrosyl [8] complexes. The spectra of a number of ruthenium and osmiumoctaethylporphyrin complexes have been examined by Gouterman *et al.* [8] and the similar broadening of $[Os(OEP)(N_2)THF]$ may be attributed to low-energy forbidden (d, π^*) transitions. The comparison of NO^+–N_2Ar^+binding on the one hand and the ArN^+–N_2 analogy on the other has been the subject of much discussion [3]. The use of macrocyclic derivatives allows for ready comparisons between these species where the isostructural series can be prepared, as in this case.

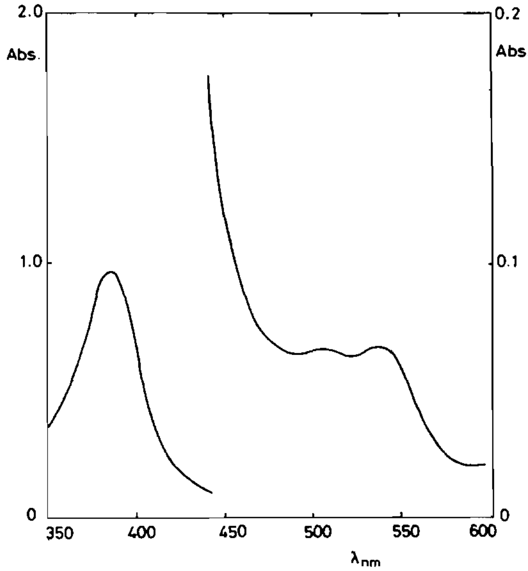


Fig. 1. Visible spectrum of $[Ru(OEP)(p\text{-}NO_2C_6H_4N_2)(EtOH)]BF_4$.

We have begun to examine some reactions of these species, both from the point of view of the ArN_2^+–N_2 analogy and as precursors for other ruthenium–porphyrin species. In pyridine the known complexes $(Ru(porp)py_2)$ were formed. The observation [11] that $[Ru(CO)_2(N_2Ph)(PPh_3)_2]^+$ reacts with BH_4^- in presence of phosphine prompted us to attempt a similar reaction. However, both for TPP and OEP derivatives the only product isolated from the reaction with BH_4^- in ethanol was [Ru(Porp)(CO)EtOH], as judged by their characteristic infrared and visible spectra [1, 2]. The propensity for Ru(II) to abstract CO from organic molecules is well known and recently the catalytic decarbonylation of aldehydes by ruthenium–porphyrin complexes has been reported [12]. A possible mechanism in our case is formation of the unsatured Ru(II)–porphyrin species followed by CO abstraction from solvent.

These and other aspects of the chemistry of the reported complexes are under investigation and will be reported subsequently.

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References

1 B. C. Chow and I. A. Cohen, *Bioinorg. Chem., 1,* 57 (1971).
2 M. Tsutsui, D. Ostfeld and L. M. Hoffman, *J. Am. Chem. Soc., 93,* 1820 (1971).
3 D. Sutton, *Chem. Soc. Rev., 4,* 663 (1975).
4 J. V. McArdle, A. J. Schultz, B. J. Corden and R. Eisenberg, *Inorg. Chem., 12,* 1676 (1973).
5 K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc. Dalton,* 2713 (1973).
6 W. L. Bowden, W. F. Little and T. J. Meyer, *J. Am. Chem. Soc., 95,* 5084 (1973).
7 J. Colin, G. Butler and R. Weiss, *Inorg. Chem., 19,* 3828 (1980).
8 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc., 100,* 3015 (1978).
9 N. Farrell, D. Dolphin and B. R. James, *J. Am. Chem. Soc., 100,* 324 (1978); M. A. Cairns, D. Dolphin and B. R. James, private communication.
10 F. R. Hopf and D. G. Whitten, *J. Am. Chem. Soc., 98,* 7422 (1976).
11 B. L. Haymore and J. A. Ibers, *Inorg. Chem., 14,* 2784 (1975).
12 G. Domazetis, B. Tarpey, D. Dolphin and B. R. James, *J. Chem. Soc. Chem. Comm.,* 939 (1980).