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Synthesis and Electrochemical Behaviour of Novel Ruthenium(II) Tetraphenylporphinate Derivatives

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The reaction of [RuTPP(CO)] (TPP = meso-tetraphenyl porphinate dianion) with several monodentate ligands L (L = t-butyl isocyanide, triphenylphosphine, dimethylphenylphosphine, triethylphosphine, trimethylphosphite) yields novel ruthenium(II) derivatives of formula [Ru(TPP)L$_2$], characterized by their visible, i.r. and ^{1}H n.m.r. spectra.

The electrochemical behaviour of these complexes in a CH$_3$CN–benzene 50% (v/v) mixture with TBAP or TBATFB as supporting electrolyte, has been studied by employing cyclic voltammetry and controlled potential electrolysis.

Both the first anodic and the first cathodic process observed involves an electron transfer at the central metal yielding ruthenium(III) and ruthenium(I) derivatives. The potentials related to these processes are strongly dependent on the nature of the ligand L. The influence of the π-bonding abilities of the ligand on the stabilization of the different oxidation states is discussed.

Introduction

In the recent years increasing interest has been focused on the Fe^{II} porphyrins because of the biological significance of the naturally occurring iron porphyrins.

Electrochemical studies on hexacoordinated Fe^{III} porphines [1, 2] showed that the first reduction process is always monoelectronic and reversible in character. The controlled potential oxidation of porphine derivatives of several metals in aprotic media, followed by e.p.r. measurements of the solutions, showed that in the case of iron(II), cobalt(II) and nickel(II) [3] the central metal is involved in the electron exchange process, while in the case of zinc(II), magnesium(II) and copper(II) derivatives [3, 4] it is the porphine ring which undergoes a one electron oxidation.

The ease of oxidation and the paramagnetism very often found in iron(II) compounds shifted the interest on the ruthenium(II) analogues, which do not present these nuisances.

The anodic behaviour on a platinum electrode of [Ru(TPP)LL′] derivatives (TPP = tetraphenylporphinate dianion; L = L′ = CO or L = CO and L′ = pyridine) seems to indicate that, when at least one axial position is occupied by carbon monoxide, the porphyne ring is involved in the oxidation process [5]. On the contrary, in the case of analogous complexes of osmium(II), the oxidation site is always the central metal [6].

In order to ascertain the influence of the axial ligands on the redox potentials of the [Ru(TPP)L$_2$] complexes, we have studied the cathodic and anodic processes which undergo, in aprotic media, the novel derivatives, synthesized by us, with the ligands L = t-butyl isocyanide, triphenylphosphine, dimethylphenylphosphine, triethylphosphine and trimethylphosphite.

Experimental

Chemicals

Reagent grade acetonitrile was further purified by distilling repeatedly from phosphorus pentoxide and storing on molecular sieves (3 Å) under nitrogen atmosphere. Reagent grade benzene was stored on sodium wire in a nitrogen atmosphere.

The supporting electrolytes tetrabutylammonium perchlorate (TBAP) and tetrafluoroborate (TBATFB), prepared by neutralizing tetrabutyl-

TABLE I. Analytical and Vis. Spectral Data.

Compound	C%		H%		N%		Spectral Data[a]; λ(ε)
	calcd	found	calcd	found	calcd	found	
$[Ru(TPP)(PEt_3)_2]$	70.79	70.5	6.15	5.85	5.90	6.1	$421(6.5 \times 10^4)$; $437(1.45 \times 10^3)$ $525(9.3 \times 10^3)$; $561(5.2 \times 10^3)$
$[Ru(TPP)(PMe_2Ph)_2]$	72.78	72.5	5.09	4.9	5.66	5.7	$433(2.0 \times 10^5)$; $524(8.4 \times 10^3)$ $555(5.1 \times 10^3)$
$[Ru(TPP)(PPh_3)_2]$	77.59	77.2	4.72	5.0	4.52	4.4	$419(8.2 \times 10^4)$; $512(6.3 \times 10^3)$
$[Ru(TPP)(P(OMe)_3)_2]$	62.43	61.8	4.82	4.6	5.82	5.9	$425(2.3 \times 10^5)$; $532(8.7 \times 10^3)$
$[Ru(TPP)(C_4H_9NC)_2]$	73.69	72.9	5.27	5.1	9.55	9.8	$419(3.4 \times 10^5)$; $529(9.7 \times 10^3)$

[a] Band positions in nm; ε values in parentheses.

ammonium hydroxide with the appropriate acid, were recrystallized from methanol and dried in a vacuum oven at 50 °C.

All other chemicals were of analytical reagent grade and were used without further purification.

Preparation of Ruthenium(II) Tetraphenylporphyrins

[Ru(TPP)(CO)] was prepared by standard procedure [7–9] and purified by column chromatography on acid alumina with chloroform–benzene; the solid was recrystallized from chloroform–methanol and dried under vacuum*.

The complexes $[Ru(TPP)(PEt_3)_2]$, $[Ru(TPP)(PMe_2Ph)_2]$, $[Ru(TPP)(PPh_3)_2]$, $[Ru(TPP)(P(OMe)_3)_2]$ and [Ru(TPP)(t-but-NC)$_2$] were all prepared by the following procedure: [Ru(TPP)(CO)] (1 mmol) partially dissolved in CH_2Cl_2 (~50 ml) was treated under nitrogen with an excess of the appropriate ligand (~3 mmol) under magnetic stirring. An immediate evolution of CO occurs and after 1 h the crude product is precipitated by dilution with CH_3OH. The very pure derivatives were obtained by chromatographing twice on acid alumina (grade 2) with a benzene–CH_2Cl_2 50% (v/v) mixture as eluant. The addition of methanol to the eluted solutions affords the complexes as purple crystals.

Analytical and vis. spectral data are reported in Table I.

Apparatus and Procedure

Voltammetric experiments were carried out in a three electrode cell. The working electrode was a platinum sphere in the anodic investigations, while in the cathodic ones a gold sphere freshly covered with mercury was employed. It was surrounded by a platinum spiral counter-electrode and its potential was probed by a Luggin capillary-reference electrode compartment whose position was made adjustable by mounting it on a syringe barrel.

Coulometric and preparative tests were carried out in a H-shaped cell with cathodic and anodic compartments separated by a sintered glass disk; a platinum gauze or a mercury pool was used as a working electrode, while the counter electrode was always a mercury pool. In all cases an aqueous SCE was used as reference electrode.

The employed voltammetric unit was a three electrode system assembled with the MP-System 1000 equipment in conjunction with a digital logic function generator made up in these laboratories [10]. The recording device was either a Hewlett-Packard 7040A X–Y recorder or a Hewlett-Packard memory scope type 1201A.

In the controlled potential electrolyses an Amel 557/SU potentiostat was used and the associated coulometer was an Amel 558 integrator.

E.p.r. spectra were recorded with a Varian E3 instrument; controlled potential electrolyses were made directly in the e.p.r. cavity.

The electroanalytical investigations were performed at 20 °C; the solutions were prepared by dissolving weighed amounts of the studied compounds in the degassed 0.1 *M* TBAP (or TBATFB), acetonitrile–benzene 50% (v/v) solvent. This solvent was used owing to the low solubility of the investigated complexes in pure acetonitrile.

^1H n.m.r. spectra were recorded with a Varian NV14 (60 MHz) spectrometer; i.r. and u.v.–vis. spectra were recorded in benzene solutions with a Perkin-Elmer 457 and a Beckman Acta V spectrophotometer, respectively. Elemental analyses were carried out by the Microanalytical Laboratory of the

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*This product has been reported to be [Ru(TPP)(CO)(MeOH)] [9a]. However no evidence for coordinated or free MeOH has been found in our nmr measurements and hence in this work we refer to it as [Ru(TPP)(CO)].

TABLE II. ^{1}H N.m.r. Data.^{a}

Compound	β-Pyrrolic Protons	Phenyl Protons	Characteristic Ligand Protons
[Ru(TPP)(PEt$_3$)$_2$]	8.18s (8)	7.85m (20)	−1.15q (18) (CH$_3$) −2.22m (12) (CH$_2$)
[Ru(TPP)(PMe$_2$Ph)$_2$]	8.15s (8)	7.28m (30)	−2.40t (12) (CH$_3$) J_{P-H} = 3 Hz
[Ru(TPP)(P(OMe)$_3$)$_2$]	8.38s (8)	7.75m (20)	0.85t (18) (OCH$_3$) $^3J_{P-H}$ = 3.5 Hz
[Ru(TPP)(C$_4$H$_9$NC)$_2$]	8.40s (8)	7.81m (20)	−0.45s (18) (CH$_3$)

^{a}Referred to TMS, CDCl$_3$ soln.; s = singlet, t = triplet, q = quintet, m = multiplet; values in parentheses are the integration ratios.

TABLE III. Cathodic Peak Potential Values Obtained on Hg Electrode.

Compound	E_p (c$_1$)/V	E_p (c$_2$)/V	E_p (c$_3$)/V
[Ru(TPP)(PEt$_3$)$_2$]	−1.91	−2.52	–
[Ru(TPP)(PMe$_2$Ph)$_2$]	−1.88	−2.43	–
[Ru(TPP)(PPh$_3$)$_2$]	−1.84	−2.23	−2.42
[Ru(TPP)(P(OMe)$_3$)$_2$]	−1.80	−2.20	−2.65
[Ru(TPP)(C$_4$H$_9$NC)$_2$]	−1.73	−2.11	−2.52
[Ru(TPP)(CO)]	−1.51	−1.98	−2.33

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Results and Discussion

[Ru(TPP)(CO)] reacts under very mild conditions with a wide variety of ligands such as phosphines and isocyanides leading to complete substitution of the CO in the axial position with the ligands L. It seems likely that ligands bearing strong σ-donor ability, such as phosphines, phosphites or isocyanides, do not require photochemical or thermal reaction for this substitution.

The ν(N≡C) of the coordinated isocyanides in the [Ru(TPP)(t-C$_4$H$_9$NC)$_2$] complex is very low (ν(N≡C) = 2106 cm^{-1}); it is lower than in the pure isocyanide, thus indicating a quite high electron density on the central metal and hence a quite important back bonding from the central metal to the axial ligands. This fact could explain the easy oxidation to ruthenium(III) and the instability of the ruthenium(I) derivatives presently found for this complex, as will be reported later.

The ^{1}H n.m.r. data, reported in Table II, show, as far as the ligand resonances are concerned, a strong upfield shift due to the porphyrin ring current. This fact has been already observed in ruthenium(II) porphyrin–imidazole derivatives [7] and in other metal–porphyrin complexes [11].

Ruthenium(II) Complexes Reduction

The cathodic behaviour of the ruthenium(II) complexes was studied at a stationary mercury microelectrode in acetonitrile–benzene solutions (50% v/v) by cyclic voltammetry. All the complexes investigated exhibited three cathodic peaks with the exception of [Ru(TPP)(PMe$_2$Ph)$_2$] and of [Ru(TPP)(PEt$_3$)$_2$] whose third reduction step could not be observed probably because it falls at more negative potentials than the solvent discharge. The corresponding peak potential values are collected in Table III.

As a typical voltammetric picture obtained on the investigated complexes, Fig. 1 shows the cathodic behaviour exhibited by solutions of [Ru(TPP)(CO)]. It can be seen that on the reverse scan two anodic peaks, a$_1$ and a$_2$, are observed which appear to be associated with c$_1$ and c$_2$ respectively, as shown by suitable restriction of the range of the potential scan. On the contrary no anodic peak associated with the third cathodic one, c$_3$, was observed even employing high scan rates. A similar voltammetric behaviour was found for the other ruthenium(II) complexes.

The first cathodic process, for all the investigated complexes, was found to involve one electron by comparison of the peak heights measured for solutions of the complexes with that of 9,10-diphenylanthracene and of [Ni(CN)$_2$(PEt$_2$Ph)$_2$] for which the occurrence of a one electron reduction process has been shown unambiguously [12, 13].

The linear dependence both of the peak current on the square root of the scan rate (30 mV s^{-1}–3 V

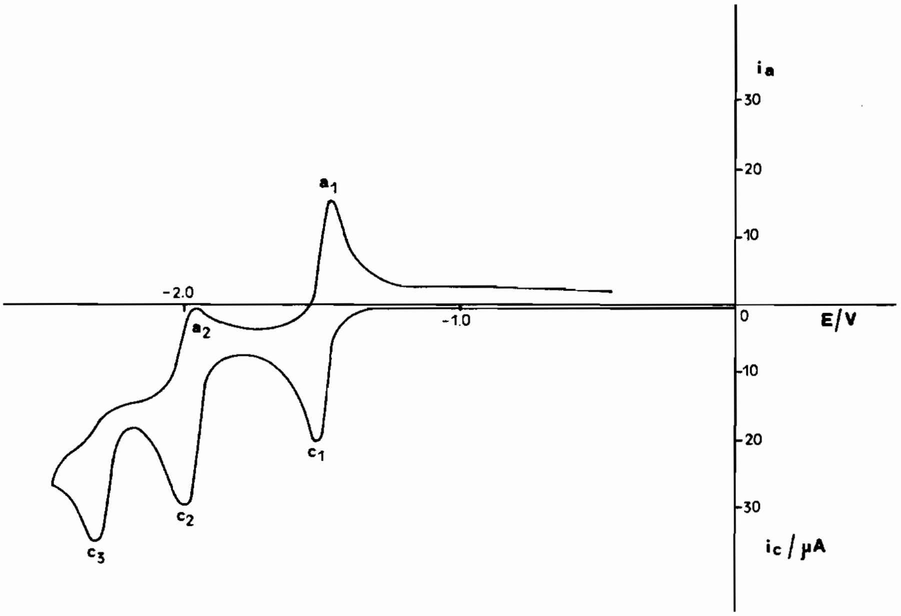

Fig. 1. Cyclic voltammetric curve recorded on a mercury coated gold microelectrode in a 5 × 10^{-4} *M* [Ru(TPP)(CO)], 0.1 *M* TBAP, CH_3CN–C_6H_6 (50% v/v) solution. Scan rate 0.2 V s^{-1}.

s^{-1}) in voltammetric tests and of the instantaneous current on the square root of the time in chronoamperometric experiments, indicate the diffusive character of the first reduction process in all cases. It could also be observed that the E_p values for peaks c_1 did not shift towards more cathodic potentials on increasing the scan rate thus indicating that the process involved is reversible. This reversibility was confirmed on measuring both the ΔE_p values between the cathodic and the associated anodic peaks a_1 and the difference between the E_p and the $E_{p/2}$ values relative to each cathodic peak c_1; in both cases 60 mV were always obtained.

In cyclic voltammetric tests it could also be noted that the ratio between the height of the anodic peak a_1 and that of the corresponding cathodic peak c_1 was equal to one even at low scan rates (30 mV s^{-1}) for all the complexes, thus indicating that the primary reduction products do not undergo chemical decay under the employed experimental conditions.

As all the investigated complexes exhibited the same voltammetric behaviour, it seems worthwhile to point out that this finding makes possible a reliable correlation of the reduction potentials and the effect of the extraplanar ligands.

In order to test whether in the reduction reaction:

$$[Ru(TPP)L_2] + e^- \rightleftharpoons [Ru(TPP)L_2]^-$$

the electron is transferred from the electrode to the central atom or to the porphyrin ring, electron spin resonance spectra were recorded by carrying out controlled potential electrolyses directly in the e.p.r. cavity. No absorption could be detected for all the complexes investigated, at variance with that observed when e.p.r. spectra were run on tetraphenylporphyrin solutions in the same experimental conditions. In this last case, an intense signal at 3385 ± 25 G could be detected according to the literature [14]. It is hence probable that the reduction reaction involves the metal, in good agreement with what is found for several other metalloporphyrin radicals [15]. In fact in this case the ruthenium(I) derivatives have a d^7 configuration probably with a spin value higher than ½ and hence very low relaxation times. No e.p.r. signal has been detected in the case of [Ru(TPP)(CO)] either, in disagreement with previously published findings [5]. Recent work has shown that in the case of the [Os(OEP)(CO)(py)] complex the first oxidation process involves the Os atom [6].

Controlled potential coulometric experiments, carried out at potential values corresponding to the first cathodic peak, showed that in all cases the current did not drop to a negligible value after the passage of one mol of electrons per mol of depolarizer. This result is in apparent disagreement with the voltammetric data which indicates that only one electron is involved in the first reduction step; it suggests that the electrode reduction product is involved in a relatively slow chemical reaction (insignificant on the time scale of the voltammetric experiments) which regenerates the electroactive species, ruthenium(II). The hypothesis of a catalytic nature of the electrode reaction is supported both by the coulometric data, since the current remained practically unchanged

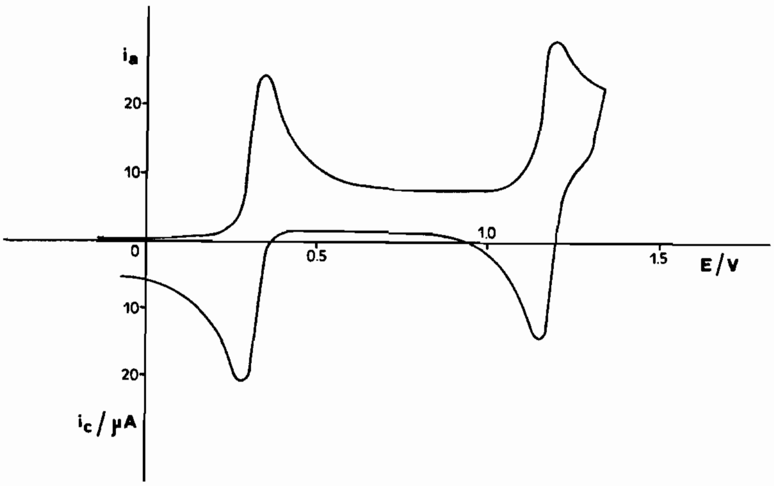

Fig. 2. Cyclic voltammetric curve recorded on a platinum microelectrode in a 5 × 10^{-4} *M* [Ru(TPP)(PEt$_3$)$_2$], 0.1 *M* TBAP, CH_3CN–C_6H_6 (50% v/v) solution. Scan rate 0.2 V s^{-1}.

even after the passage of a considerable number (10–15) of mol of electrons per mol of depolarizer, and by the voltammetric behaviour of the electrolyzed solutions. In fact the voltammetric picture, and in particular the height of the first cathodic peak, did not appear to be substantially modified during these electrolyses.

In order to gain information about the species which is responsible for the chemical re-formation of the depolarizer during the controlled potential electrolyses, special attention was paid to the effects caused by changes in supporting electrolyte and to the influence of small amounts of water. By using tetrafluoroborate as supporting electrolyte, rather than perchlorate, it could be observed, in fact, that the current, during controlled potential reductions carried out in correspondence to the first cathodic process, decreased with time. Moreover, voltammetric tests performed after these reductions revealed the presence in solution of the species responsible for the anodic peak a_1. However, even in these experimental conditions, the species [Ru(TPP)L$_2$]$^-$ did not appear to be stable; in fact the peak a_1 decayed with time and disappeared in about 10 minutes while at the same time the peak c_1 increased up to its initial height. By adding small amounts of water to the solution containing TBATFB as supporting electrolyte, we could observe a substantial similarity in coulometric results with those obtained in presence of TBAP. However we believe that a possible higher content of water in TBAP, with respect to TBATFB, was not responsible for the different behaviour observed in presence of the two supporting electrolytes. In fact, in the experiments in which TBAP was employed, special care was taken to exclude water, including drying the solvent with CaH_2, baking all glassware and supporting electrolyte in a vacuum, making all transfers out of contact with the atmosphere and operating under a blanket of purified nitrogen. We suggest, therefore, that the species [Ru(TPP)L$_2$]$^-$ electrochemically produced, is reoxidized either by perchlorate anion of the supporting electrolyte or by protic species present in solution. This is in agreement with the expected relative instability of the ruthenium(I) derivatives; in this connection it must be remarked also that the reoxidation of the cathodic product operated by perchlorate ions has been found by other workers [16–18].

As far as the second cathodic peak is concerned, it was possible to observe that its height did not depend linearly on the square root of the potential scan rate, but the ratio $i_p/v^{1/2}$ decreased on increasing the scan rate. Moreover, in the controlled potential electrolyses, carried out in correspondence of the second cathodic process, the current remained again practically unchanged even after the passage of a considerable number of mol of electrons per mol of depolarizer. These findings suggest that also at these potential values a catalytic process is involved. However, on considering the instability of the product obtained in correspondence of the first cathodic peak, which is probably the depolarizer of the second reduction process, no further investigation was carried out. For the same reason the process occurring at the third cathodic peak was neither investigated.

Ruthenium(II) Complexes Oxidation

All the ruthenium(II) complexes, investigated on a platinum microelectrode in acetonitrile–benzene solutions (50% v/v), exhibited two anodic peaks the potentials of which are collected in Table IV. As typical cyclic voltammetric picture obtained on the

TABLE IV. Anodic Peak Potential Values Obtained on Pt Electrode.

Compound	$(E_p)_1/V$	$(E_p)_2/V$
$[Ru(TPP)(PEt_3)_2]$	0.36	1.21
$[Ru(TPP)(PMe_2Ph)_2]$	0.45	1.22
$[Ru(TPP)(PPh_3)_2]$	0.50	1.24
$[Ru(TPP)(P(OMe)_3)_2]$	0.59	1.25
$[Ru(TPP)(C_4H_9NC)_2]$	0.65	1.26
$[Ru(TPP)(CO)]$	0.93	1.27

investigated complexes, Fig. 2 shows the anodic behaviour exhibited by solutions of $[Ru(TPP)(PEt_3)_2]$. In all cases, both anodic peaks observed were found to be monoelectronic, diffusive in character and perfectly reversible on the basis of the arguments cited above for the cathodic peaks. Moreover the ratio between the height of the anodic peaks and that of the associated cathodic ones, equal to one at any scan rate, indicated that the anodic product, $[Ru(TPP)L_2]^+$, did not decay under the employed experimental conditions. However, e.p.r. spectra, recorded on ruthenium(II) solutions directly oxidized in the cavity of the instrument in correspondence to the first anodic peak, did not exhibit any signal. As porphyrin solutions, under the same conditions, exhibit a strong e.p.r. signal [3], it seems likely that the central atom is also involved in the oxidation process. On the other hand the lack of any e.p.r. signal in the oxidized solutions of ruthenium(II) is in agreement with the results found for transition metal complexes in the d^5 configuration [19].

Controlled potential coulometric experiments, carried out at potential values corresponding to the first anodic peak, showed that in all cases the current dropped to negligible values for $n_e = 1$. Cyclic voltammetric tests performed on the electrolyzed solutions allowed to verify the good stability of the anodic product under a nitrogen atmosphere; unfortunately our attempts to isolate the oxidation products from the solutions were unsuccessful because of the porphyrin ring oxidation which occurred during the work-up.

Controlled potential coulometric experiments carried out in correspondence of the second anodic peak, gave a n_e value higher than two in apparent disagreement with the voltammetric findings. The nature of the slow chemical reaction which affects the coulometric data but is insignificant on the time scale of the voltammetric experiments has not been investigated. However, the values of the peak potentials were practically the same, thus suggesting that for all the complexes the porphyrin ring is involved in the second oxidation step.

The comparison of both the cathodic and the anodic peak potentials shows a marked influence of the nature of the axial ligands when the redox process involves the central metal (first anodic and cathodic peak). In fact, ligands with a good π-bonding ability, such as CO and t-butyl isocyanide, stabilize the porphine derivatives in the lower valence state (cathodic sequence), while making the complexes oxidizable at higher potentials (anodic sequence). On the opposite side, good σ-donor ligands, such as triethylphosphine, make the derivatives easier to oxidize and then destabilize the anionic complex.

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