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Preliminary communication

Novel organometallic charge transfer salts derived from electron-rich diruthenium species and the electron-acceptor ligands 7,7,8,8-tetracyano-*p*-quinodimethane and tetracyanoethylene and containing the radical anions of these ligands in both the inner and the outer coordination spheres

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Abstract

Reaction of the electron-rich diphosphazane-bridged diruthenium complexes $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or ^iPr) with the electron-acceptor ligands 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, and tetracyanoethylene, TCNE, results in electron transfer and the formation of the charge transfer salts $[Ru_2(CO)_5(TCNX)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]TCNX$ (X = Q or E) containing the radical anion of the electron-acceptor ligand in both the inner and the outer coordination spheres.

An area of study of continuing interest is that involving radical anion salts derived from electron-rich organic and organometallic compounds and electron-acceptor ligands such as 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, and tetracyanoethylene, TCNE. This stems from the fact that many of these species possess novel conducting and magnetic properties [1]. The TCNX (X = Q or E) ligand in many of these salts is found as either a partially or fully reduced, but non-co-ordinated, species, *i.e.* the ligand occupies the outer co-ordination sphere of the donor cation as in $[Fe(\eta^5\text{-}C_5Me_5)_2]TCNQ$ for instance [2]. Also of considerable interest, however, are those complexes in which the TCNX ligand is bonded in the inner co-ordination sphere, recent examples being provided by $[\{Mn(\eta^5\text{-}C_5R_5)(CO)_2\}_n(\mu,\eta^n\text{-}TCNX)]$ (R = H or Me, n = 1–4) [3] and $[\{Re_2Cl_4(\mu\text{-}Ph_2PCH_2PPh_2)_2\}_2(\mu\text{-}TCNQ)]$ [4]. We now wish to report a range of charge transfer salts derived from dinuclear electron-rich species and TCNX (X = Q or E)

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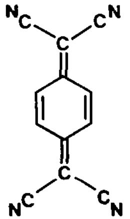
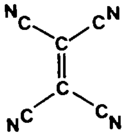
containing the radical anions of the TCNX ligands in both the inner and the outer coordination spheres.

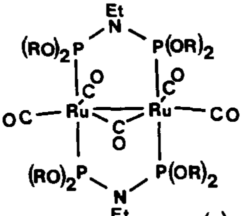


(TCNQ)

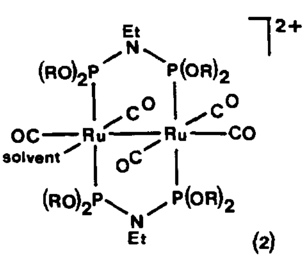


(TCNE)

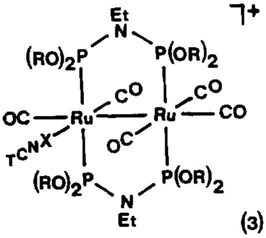
We have established previously that the diruthenium diphosphazane ligand-bridged derivatives $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (**1**) (R = Me or ^iPr) are readily oxidized, either chemically [5] or electrochemically [6], to afford, in weakly coordinating solvents, the solvento species $[Ru_2(CO)_5(solvent)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^{2+}$ (**2**). We also established that the potentials of these oxidations are more cathodic than the reduction potentials for the electron acceptor compounds TCNQ and TCNE, and on this basis it was anticipated that the latter would readily oxidize the above diruthenium compounds and in the process become co-ordinated. Indeed, addition of a toluene solution of either of the neutral dinuclear pentacarbonyl derivatives to a toluene solution of TCNQ led to the separation of a green product which on crystallization from dichloromethane/light petroleum afforded an intense dark green microcrystalline material characterized as the 1 : 1 salt $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)\text{-}P(OR)_2\}_2]TCNQ$ (R = Me or ^iPr). * The infrared spectra of these species contain a set of peaks in the terminal C–O stretching region (2050, 2030 and 1995 cm^{-1} for R = ^iPr, measured in CH_2Cl_2) whose band pattern is essentially the same as that observed for cations of the type $[Ru_2(CO)_5(\eta^1\text{-ligand})\{\mu\text{-}(RO)_2PN(Et)\text{-}$



(1)



(2)



(3)

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* Satisfactory microanalyses were obtained for all new compounds synthesized.

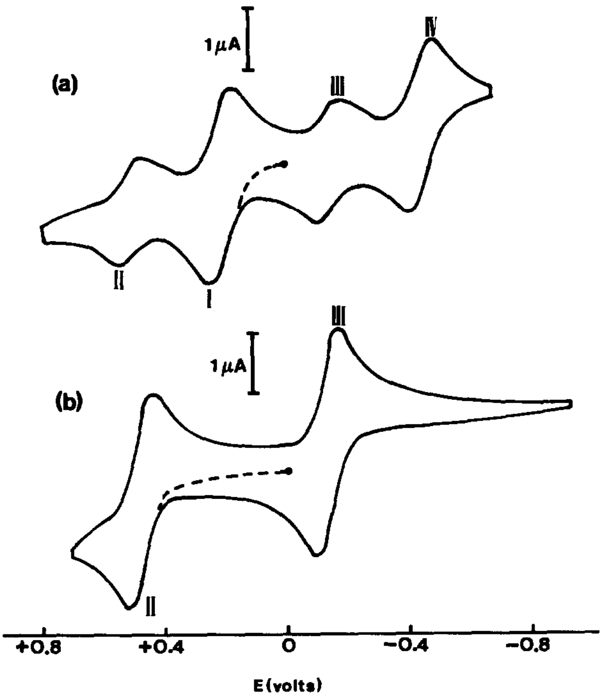

Fig. 1. Cyclic voltammograms in benzonitrile ($\sim 1.0 \times 10^{-3}$ M in compound) at 25°C at a scan rate of 200 mV/sec (0.1 M TBAP; platinum disc working electrode) of (a) $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]TCNQ$ and (b) $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]BPh_4$. $E_{1/2}$ values: I, 0.19; II, 0.49; III, −0.17; IV, −0.47 V *vs* Ag/AgCl.

$P(OR)_2\}_2]^{n+}$ [7,8]. The stereochemistry of a number of these cations and the benzonitrile species $[Ru_2(CO)_5(\eta^1\text{-}PhCN)\{\mu\text{-}({}^iPrO)_2PN(Et)P(O^iPr)_2\}_2]^{2+}$ in particular [8], have been established X-ray crystallographically and it is proposed, on the basis of the IR spectral evidence, that the carbonyl and TCNQ ligands in (**3**; X = Q) are arranged similarly. Three bands which can be assigned to a coordinated TCNQ ligand (*vide infra*) are observed in the C≡N stretching region of the IR spectra of these species (2195, 2150 and 2100 cm^{-1} for R = ${}^iPr$, measured in CH_2Cl_2). Four bands are theoretically expected in this region for a TCNQ ligand which is coordinated through one of its nitrogen atoms, *i.e.* in the η^1-coordination mode but presumably the fourth band is obscured by overlap as indeed is often found to be the case [9,10]. A further and much stronger C≡N stretching band (2180 cm^{-1} for R = ${}^iPr$, measured in CH_2Cl_2) confirms the presence of a free $TCNQ^-$ anion in the salt; the C≡N stretching vibration for $TCNQ^-$ in KTCNQ absorbs at 2183 cm^{-1} [11]. Also consistent with the proposed stereochemistry of the $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ cations are the low temperature ${}^{31}P\{{}^1H\}$ NMR spectra which exhibit an AA′BB′ pattern of peaks indicative of two sets of chemically equivalent phosphorus atoms. The cyclic voltammograms (CV's) of these compounds (Fig. 1(a)) contain four reversible one-electron waves two of which (I and IV) correspond with those observed in the CV of LiTCNQ indicating the presence of both a non coordinated and a coordinated TCNQ ligand (*vide infra*).

With the aim of establishing unequivocally the presence of both coordinated and free TCNQ in these salts, their TCNQ anions were replaced metathetically by tetraphenylborate anions to afford products characterized as $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]BPh_4$ (R = Me or ^{i}Pr). The IR spectra in the C–O stretching region and the low temperature $^{31}P\{^1H\}$ NMR spectra of these tetraphenylborate derivatives were identical with those of the corresponding TCNQ salts, as indeed were the bands in the C≡N stretching region in all respects but one; the strong peak at 2180 cm^{-1}, assigned to the $TCNQ^{\cdot-}$ anion, was no longer present. Moreover, the CV's of these species exhibited only two reversible waves (Fig. 1(b)) which correspond with waves II and III in the CV's of $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]TCNQ$. The separation between waves II and III is essentially the same as that between waves I and IV of the free $TCNQ^{\cdot-}$ anion, an observation which strongly suggests that the former arise from redox changes associated with the coordinated TCNQ ligand rather than with the ruthenium atoms. On this basis wave II is assigned to the $L_nRu_2\text{-}TCNQ^0/L_nRu_2\text{-}TCNQ^{\cdot-}$ couple and wave III to the $L_nRu_2\text{-}TCNQ^{\cdot-}/L_nRu_2\text{-}TCNQ^{2-}$ couple where L_n denotes the co-ligands. It is also concluded that the co-ordinated TCNQ ligands in both $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]TCNQ$ and $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]BPh_4$ coordinate as a radical anion to a diamagnetic formally co-ordinatively saturated ruthenium centre, *i.e.* according to formulation **B** rather than formulation **A** as shown. Indeed, the data from preliminary ESR measurements on $[Ru_2(CO)_5(TCNQ)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]BPh_4$ (R = Me or ^{i}Pr) are readily interpreted in terms of the presence of an η^1-coordinated $TCNQ^{\cdot-}$ radical anion [12]. As indicated, the co-ordinated $TCNQ^{\cdot-}$ ligand is reduced at potentials positive of those required for the reduction of the $TCNQ^{\cdot-}$ anion (Fig. 1(a)); this anodic shift is that expected when the coordinated $TCNQ^{\cdot-}$ functions as a N σ-donor ligand [3,9].

$$\underset{(\mathbf{A})}{[L_nRu_2^{+}\text{-}TCNQ^0]^+} \rightarrow \underset{(\mathbf{B})}{[L_nRu_2^{2+}\text{-}TCNQ^{\cdot-}]^+}$$

The reactions of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or ^{i}Pr) with TCNE have also been investigated and, analogous to those reactions involving TCNQ, products of the type $[Ru_2(CO)_5(TCNE)\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]TCNE$ containing TCNE ligands in both co-ordination spheres, were obtained.

To the best of our knowledge, only one other charge transfer salt containing a TCNX (X = Q or E) ligand in both its outer and its inner coordination spheres, *viz.* $[Fe(Ph_2PC_2H_4PPh_2)_2TCNE]TCNE$, has been reported previously [13]; certainly the compounds synthesized in this study are the first examples of dinuclear compounds of this type. Although all attempts to obtain single crystals of the above compounds have thus far proved unsuccessful, studies in this and related areas are continuing with the overall objective being to produce charge transfer salts of the type $[L_nM_x\text{-}TCNX]TCNX$ (M = metal; $x = 1, 2, 3$, etc.; L_n = co-ligands; X = Q or E) which adopt stacked structures in their crystalline state and, in particular, salts of this type in which the inner sphere and the outer sphere TCNX anions crystallize in the same stack.

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