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Oxidation behaviour of the unsaturated diruthenium species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(Pr^iO)_2PNEtP(OPr^i)_2\}_2]$

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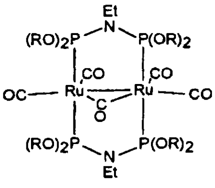
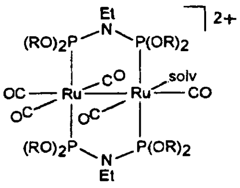
Treatment of the formally unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ [sb = semi-bridging, etipdp = $(Pr^iO)_2PNEtP(OPr^i)_2$] with silver(I) salts such as $AgSbF_6$ or $AgBF_4$ in MeCN or PhCN led directly to the formation of the disolvated species $[Ru_2(CO)_4(RCN)_2(\mu\text{-}etipdp)_2]X_2$ (R = Me or Ph; X = SbF_6 or BF_4), with no intermediates being detected. In contrast, as established spectroscopically, oxidation of this complex with silver(I) salts in very weakly co-ordinating solvents such as acetone or methanol afforded silver adducts of the parent species. Also, reaction with the electron acceptor tcnq (7,7,8,8-tetracyano-*p*-quinodimethane) in tetrahydrofuran (thf) gave the electron-transfer salt $[Ru_2(\eta^1\text{-}tcnq)(CO)_4(thf)(\mu\text{-}etipdp)_2][tcnq]$, while with *p*-chloranil (tetrachloro-1,4-benzoquinone) produced $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-}etipdp)_2][p\text{-}OC_6Cl_4O]_2$ as a consequence of the benzoquinone functioning as a chlorinating agent as well as an electron acceptor. Cyclic voltammograms of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ and $[Ru_2(CO)_4(RCN)_2(\mu\text{-}etipdp)_2][SbF_6]_2$ (R = Me or Ph) have been measured in both aceto- and benzo-nitrile and are readily interpreted in terms of the redox process $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2] + 2RCN \underset{2e}{\overset{-2e}{\rightleftharpoons}} [Ru_2(CO)_4(RCN)_2(\mu\text{-}etipdp)_2]^{2+}$. The structure of the acetonitrile species $[Ru_2(CO)_4(MeCN)_2(\mu\text{-}etipdp)_2][BF_4]_2\cdot CH_2Cl_2$ has been determined X-ray crystallographically.



R
1a Me
1b Et



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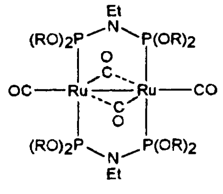


R
3a Me
3b Et

We have shown previously that the diruthenium diphosphazane-bridged complexes $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ **1** (R = Me or Pr^i),[1] substituted derivatives of thermally unstable $[Ru_2(CO)_9]$,[2] are electron rich and, as such, are readily oxidised, both electrochemically[3] and by chemical means.[4–8] Through cyclic voltammetric studies we established in particular that the oxidation of the tetramethoxydiphosphazane-bridged complex $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}etmdp)_2]$ **1a** [etmdp = $(MeO)_2PNEtP(OMe)_2$] in acetone or benzonitrile is irreversible, with the one-electron-oxidised product participating in a chemical process involving solvent attack and the product thereof being immediately oxidised to afford $[Ru_2(CO)_5(solv)(\mu\text{-}etmdp)_2]^{2+}$ **2** (solv = acetone or benzonitrile).[3] On the other hand the corresponding oxidation of the tetraisopropoxydiphosphazane-bridged species $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}etipdp)_2]$ **1b** [etipdp = $(Pr^iO)_2PNEtP(OPr^i)_2$] was found to be reversible, although further one-electron oxidation of the oxidised product $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}edipdp)_2]^+$ also proved to be irreversible, again leading to the formation of a solvated dication, *viz.* $[Ru_2(CO)_5(solv)(\mu\text{-}etipdp)_2]^{2+}$ **2** (solv = acetone or benzonitrile).[3] Significantly, although the chemical oxidation of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ **1** by silver(I) salts in appropriate solvents also afforded the solvated product, the process was shown to occur *via* the inner-sphere complex $[Ru_2(\mu\text{-}AgL)(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]^+$ (L = acetone, benzonitrile, *etc.*) as intermediate.[6] This silver(I) adduct is unstable in solution degrading with loss of elemental silver to the one-electron-oxidised product, $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]^+$, which, in turn, disproportionates in solution to the solvated species $[Ru_2(CO)_5(solv)\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]^{2+}$ **2** and the neutral compound **1**. Solvated species of type **2** (solv = acetone or H_2O) have proved to be excellent precursors for the synthesis of products involving the displacement of the co-ordinated solvent by a variety of nucleophilic reagents.[6]

We recently reported that, under appropriate reaction conditions, the pentacarbonyl species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ **1** can be decarbonylated to the formally co-ordinatively unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ **3** (sb = semibridging) which, not surprisingly, is highly reactive towards nucleophilic as well as electrophilic attack.[9] A study was thus initiated with the object of comparing the redox behaviour of the unsaturated species **3** and, in particular, its reactivity with the one-electron oxidant Ag^I and the electron acceptors tcnq (7,7,8,8-tetracyano-*p*-quinodimethane), tcne (tetracyanoethylene) and *o*- and *p*-chloranil (tetrachloro-1,2- and 1,4-benzoquinone) with that of the co-ordinatively saturated species **1**. Owing to the difficulty in obtaining workable yields of the tetramethoxydiphosphazane-bridged species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etmdp)_2]$ **3a**, the study was restricted to the tetraisopropoxydiphosphazane-bridged derivative $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$ **3b**.

Results and Discussion

Chemical oxidation of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-}etipdp)_2]$

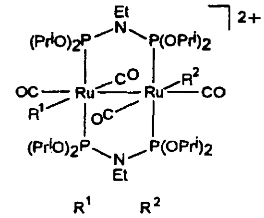
(*i*) With silver(I) salts. Not surprisingly, on the basis of previous studies involving the pentacarbonyl species **1**,[6] the

J. Chem. Soc., Dalton Trans., 1996, Pages 1031–1037

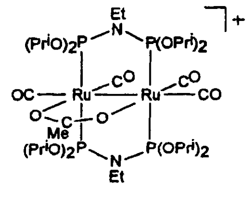
unsaturated species **3b** also proved to be susceptible to attack by silver(I) ions with the product again being found to be dependent on the nature of the ligand co-ordinated to the silver(I) ion and on the stoichiometry of the reaction. For instance, treatment with a two-fold molar equivalent of $AgSbF_6$ in acetonitrile leads to the precipitation of elemental silver and the formation of a product characterised as $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$ **4a**; the corresponding bis(benzonitrile) complex $[Ru_2(CO)_4(PhCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$ **4b**, is produced when benzonitrile is employed as solvent while the hexafluorophosphate and tetrafluoroborate salts are obtained when $AgPF_6$ and $AgBF_4$ are used as one-electron oxidants. The infrared spectra of **4a** and **4b** were found to exhibit very similar band patterns in the C–O stretching region as well as to contain peaks in the region *ca.* 2160–2300 cm^{-1} readily assigned to the C–N stretching modes of co-ordinated nitrile ligands. The ^1H NMR spectra of these salts indicated, on the basis of the integrated intensities of the resonances associated with the protons of the nitrile ligands compared with those of the protons of the diphosphazane ligands, the presence of two nitrile ligands per cation. Furthermore, their $^{31}P\text{-}\{^1H\}$ NMR spectra, measured at low (−96 °C), as well as at room temperature, were found to contain a single singlet illustrating the equivalence of the four phosphorus atoms and a symmetrical structure.

Organonitrile ligands are normally weakly co-ordinated to transition metals in lower formal oxidation states such that they can be readily displaced by other donors under mild conditions. Thus, addition of a large excess of benzonitrile to the acetonitrile derivative $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$ **4a**, in acetone at room temperature results in the displacement of the co-ordinated acetonitrile by benzonitrile affording **4b**, in near-quantitative yield; several hours were required for the reaction to go to completion. Significantly, on monitoring this reaction by means of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, a relatively stable intermediate, which exhibited a singlet at room temperature and an AA'BB' pattern of peaks at −96 °C, was detected. Furthermore, the chemical shift of this singlet was midway between those for the corresponding singlets for **4a** and **4b**. The intermediate is thus proposed to be the mixed acetonitrile–benzonitrile derivative $[Ru_2(CO)_4(MeCN)(PhCN)(\mu\text{-etipdp})_2][SbF_6]_2$ **4c**. Treatment of **4b** with an excess of acetonitrile in acetone was similarly found to afford **4a**, again *via* **4c** as intermediate. These studies confirm that the nitrile ligands of species **4** are bound fairly weakly to the ruthenium atoms and may be readily displaced. Indeed, treatment of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2]^{2+}$ with acetate ions was found to give the acetate-bridged species $[Ru_2\{\mu\text{-OC(Me)O}\}(CO)_4(\mu\text{-etipdp})_2]^+$ **5**, synthesised previously by treatment of compound **1b** with silver acetate and characterised as the hexafluorophosphate salt by means of X-ray crystallography as well as by conventional methods.[10] Passage of carbon monoxide through a solution of **4a** in acetone at room temperature results, on the other hand, in displacement of only one of the acetonitrile ligands, affording a pentacarbonyl species of type **2** $[Ru_2(CO)_5(MeCN)(\mu\text{-etipdp})_2]^{2+}$, produced previously by oxidation of **1b** in acetonitrile by silver(I) salts as described above.[6]

It has been shown previously that for the solvated pentacarbonyl species $[Ru_2(CO)_5(solv)\{\mu\text{-(RO)}_2PNEtP(OR)_2\}_2]^{2+}$ the co-ordinated solvent is much more readily displaced where the solvent is an oxygen-donor ligand, such as acetone or water, rather than one where it is a nitrogen-donor ligand such as an organonitrile or pyridine.[6] Attempts were thus made to synthesise dicationic disolvated species of the type $[Ru_2(CO)_4(solv)_2(\mu\text{-etipdp})_2][SbF_6]_2$ which contain co-ordinated oxygen-donor solvents such as acetone, methanol or tetrahydrofuran. Treatment of an acetone solution of $[Ru_2(\mu_{sb}\text{-CO})_2(CO)_2(\mu\text{-etipdp})_2]$ with an equimolar amount of $AgSbF_6$ in acetone resulted in the formation of a deep red solution and the separation of metallic silver, albeit in low yield. The product responsible for the red colour could not be isolated sufficiently pure for characterisation purposes but some evidence as to its nature was obtained from the NMR spectroscopic data. In particular its $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibited a doublet at δ 143.9 which is interpreted in terms of the formation of a silver adduct of symmetrical structure, the doublet arising from the coupling of four equivalent phosphorus nuclei with the silver(I) nucleus of spin $\frac{1}{2}$ [^2J(Ag–P) = 15.2 Hz]. Significantly the chemical shift of this doublet is consistent with the complex being monocationic.[11] A possible formulation for this cationic species is $[Ru_2\{\mu\text{-Ag(Me}_2CO)\}(CO)_4(\mu\text{-etipdp})_2]^+$ with its formation resulting from the insertion of the solvated silver(I) ion across the two ruthenium atoms of the neutral parent **3b**. Addition of a second mole equivalent of $AgSbF_6$ to the red solution led to further separation of metallic silver, in greater quantities than that observed for the initial addition, and a change of the solution from red to yellow. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the mixture indicated that a number of products had been formed but that the major one exhibited a doublet at δ 120.5 which is again interpreted in terms of the formation of a silver adduct of symmetrical structure [^2J(Ag–P) = 14.3 Hz]; the chemical shift in this instance is consistent with the formation of a dicationic species.[11] Significantly, addition of benzonitrile to the yellow solution resulted in the generation of $[Ru_2(CO)_4(PhCN)_2(\mu\text{-etipdp})_2]^{2+}$. The reaction of **3b** with $AgSbF_6$ in methanol was also investigated. A mixture of products was again found to be formed for the 1 : 2 reaction according to the $^{31}P\text{-}\{^1H\}$ NMR spectral evidence, with the major one exhibiting a doublet at δ 119.1 [^2J(Ag–P) = 15.5 Hz].



	R^1	R^2
4a	MeCN	MeCN
4b	PhCN	PhCN
4c	MeCN	PhCN



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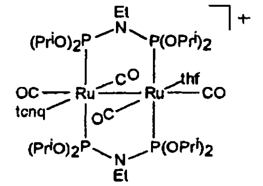

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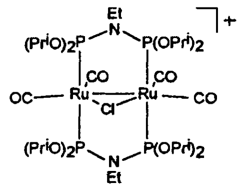

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***(ii)* With 7,7,8,8-tetracyano-*p*-quinodimethane and tetracyanoethylene.** Addition of $[Ru_2(\mu_{sb}\text{-CO})_2(CO)_2(\mu\text{-etipdp})_2]$ to a twice molar equivalent of 7,7,8,8-tetracyano-*p*-quinodimethane, both in tetrahydrofuran (thf), resulted in the formation of an intense emerald-green solution from which a dark green material, characterised by means of elemental analysis and IR spectroscopy, as the electron-transfer salt $[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2][tcnq]$ **6**, and not the expected neutral species $[Ru_2(\eta^1\text{-tcnq})_2(CO)_4(\mu\text{-etipdp})_2]$, was isolated. The IR spectrum of this species exhibits a band pattern in the C–O stretching region typical of compounds of the type $[Ru_2(CO)_4L_2(\mu\text{-etdp})_2]^{n+}$ containing equatorially co-ordinated ligands L *trans* disposed with respect to each other, indicating a related stereochemistry for **6**. Two peaks, at 2189 and 2146 cm^{-1} (measured in CH_2Cl_2), could be assigned to the C–N stretching modes of a non-co-ordinated tcnq and a co-ordinated tcnq radical anion respectively. Significantly, **6** is only the third example of a complex type containing a tcnx radical anion in both the inner and outer co-ordination spheres of the cations, the other two being the pentacarbonyl species $[Ru_2(\eta^1\text{-tcnx})(CO)_5\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2][tcnx]$ (x = e or q)[7] and $[Fe(Ph_2PC_2H_4PPh_2)_2(\eta^1\text{-tcne})][tcne]$.[12]

The reaction of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ with tcne was also investigated but a pure product could not be isolated.

(*iii*) **With tetrachloro-1,2- and -1,4-benzoquinone.** Previous studies in the authors' laboratories revealed that the pentacarbonyl species $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2]$ **1** reacts with the electron acceptor tetrachloro-1,2-benzoquinone with cleavage of one of the co-ordinated diphosphazane ligands, to afford $[Ru_2\{\mu\text{-}C(O)NEtP(OR)_2\}\{\eta^2\text{-}P(OC_6Cl_4O)(OR)_2\}(CO)_4\{\mu\text{-}(RO)_2PNEtP(OR)_2\}]$ (R = Me or Pr^i).[8] On the other hand $[Ru_2Cl(CO)_5\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2][p\text{-}OC_6Cl_4O]$ is formed in the corresponding reaction involving tetrachloro-1,4-benzoquinone resulting from the quinone functioning as a chlorinating agent as well as an electron acceptor.[8]

With the object of establishing the reactivity pattern of the unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ towards these electron acceptors, the tetracarbonyl was treated with a twice molar equivalent of *p*-chloranil in toluene. A brown oil separated immediately from which a yellow-brown microcrystalline material was isolated on further work-up. The full microanalytical data for this species indicated it to have the stoichiometry $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]_2$ **7**, such that the cation has either separated as a salt of the dimeric monoanion $(p\text{-}OC_6Cl_4O)_2{}^-$ or neutral $p\text{-}OC_6Cl_4O$ has cocrystallised with $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]$. The formation of 1 : 2 salts in charge-transfer reactions has been reported previously. For instance, reaction of 1,1-dimethylferrocene with tcnq yields the 1 : 2 salt $[Fe(\eta^5\text{-}C_5H_4Me)_2][tcnq]_2$.[13] The identity of the cation in **7** was established in the first instance by spectroscopic means. In particular the band pattern and frequencies of the carbonyl-stretching peaks in the IR spectrum as well as the chemical shift of the singlet in the $^{31}P\text{-}\{^1H\}$ NMR spectrum were identical to those for $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2]PF_6$ reported previously.[4] Final confirmation was achieved by converting **7** into the corresponding tetraphenylborate salt and characterising the latter fully. The salt $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]$ has been synthesised previously by slowly decarbonylating the pentacarbonyl species $[Ru_2Cl(CO)_5(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]$ described above.[8] Significantly the filtrate remaining after the separation of $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]_2$ was shown to contain $[Ru_2(\mu\text{-}Cl)Cl(CO)_3(\mu\text{-etipdp})_2]$ in low yield. The latter has been produced previously in a number of reactions including that of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ with chlorine.[9]

Cyclic voltammetric measurements

(*i*) **$[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$.** Cyclic voltammograms of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ **3b** were measured in both acetonitrile and benzonitrile. They were found to be very similar with that measured in acetonitrile being illustrated in Fig. 1. As shown two oxidation waves are observed on scanning anodically, with that associated with the primary oxidation being broad and irreversible and the other reversible and at a much higher potential. A broad irreversible peak (X, Fig. 1) is observed in the reverse scan. This pattern differs quite appreciably with that observed for the pentacarbonyl complex $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-etipdp})_2]$ **1b** where, as discussed above, a reversible one-electron oxidation is followed by an irreversible one-electron redox change.[3] It was not possible to determine directly the number of electrons associated with the primary oxidation but the height of the peak associated with this oxidation (MeCN as solvent: i_{pa} = 2.0 μA at 200 mV s^{-1}) is approximately double that of the primary oxidation wave in the cyclic voltammogram of an equivalent molar concentration of **1b** in MeCN (i_{pa} = 2.0 μA at 200 mV s^{-1}). Although not proof of, this observation is consistent with the primary oxidation of **3b** involving a two-electron transfer. An obvious product of such an oxidation, which would clearly involve an electrochemical–chemical–electrochemical process, is the dicationic bis-acetonitrile or -benzonitrile species $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2]^{2+}$ **4a** or $[Ru_2(CO)_4(PhCN)_2(\mu\text{-etipdp})_2]^{2+}$ **4b**, depending on the solvent employed. Confirmation that these species are indeed the products of the primary oxidation was achieved by measurement of the cyclic voltammograms of the salts of **4a** and **4b** synthesised chemically. Thus the primary reduction peak in the cyclic voltammogram of **4a** measured in acetonitrile (Fig. 2) was shown to coincide with peak X in the cyclic voltammogram of the parent compound **3b**, measured in acetonitrile. Furthermore, two anodic waves (Y and Z) were observed in the reverse scan in this cyclic voltammogram with the first oxidation wave being irreversible and the second being essentially reversible and with their potentials corresponding to the oxidation waves of the parent unsaturated complex **3b**. On the other hand, but consistent with that expected, a single primary oxidation peak is observed in the cyclic voltammogram of **4a** on scanning anodically with this peak coinciding with the second oxidation in the cyclic voltammogram of **3b**. The product of this oxidation is presumably $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2]^{3+}$. Measurement of the cyclic voltammogram of **4b** in benzonitrile produced similar results.

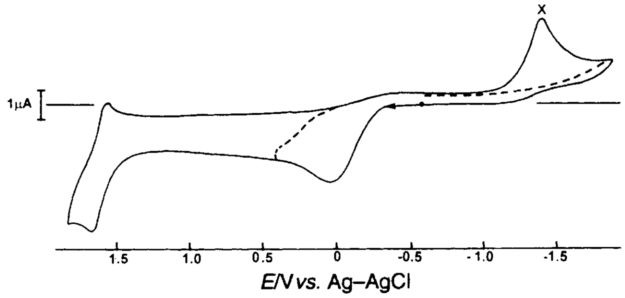


Fig. 1 Cyclic voltammogram of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ (1.0 mmol dm^{-3}) measured in acetonitrile (0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate) using a platinum working electrode (298 K, 200 mV s^{-1})

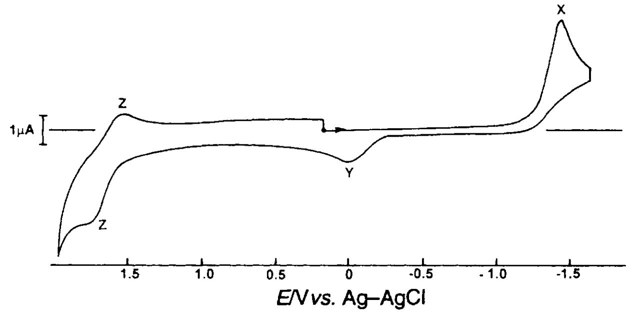
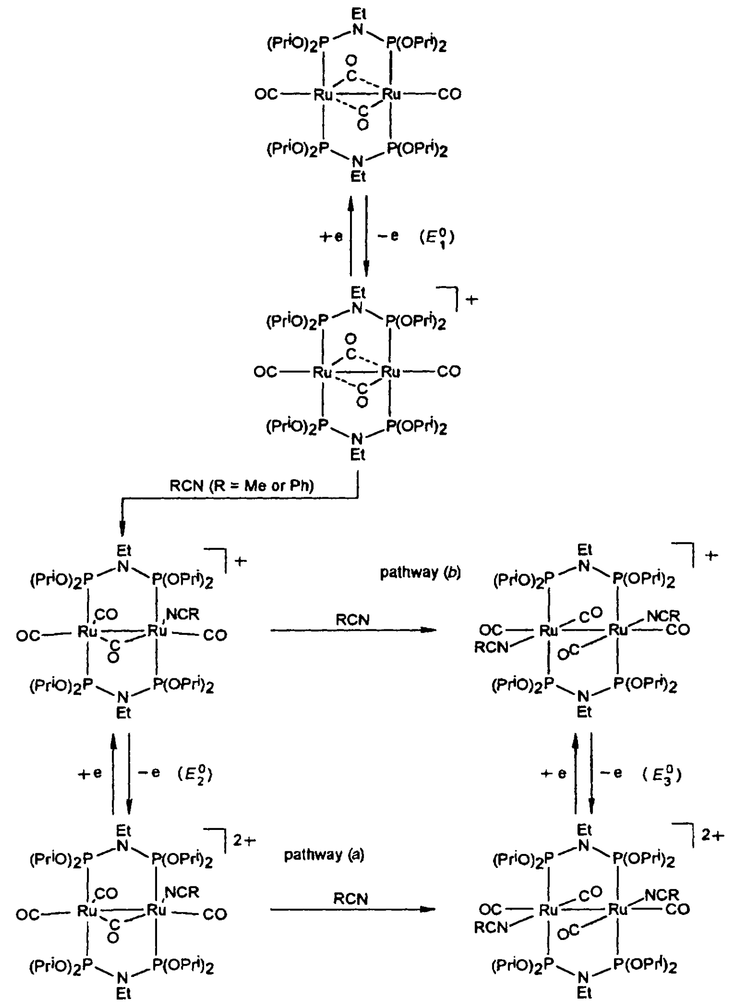


Fig. 2 Cyclic voltammogram of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$ (1.0 mmol dm^{-3}) measured in acetonitrile. Conditions as in Fig. 1

Two possible reaction pathways for the formation of $[Ru_2(CO)_4(RCN)_2(\mu\text{-etipdp})_2]^{2+}$ (R = Me or Ph) by electrochemical oxidation of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ **3b** in aceto- or benzo-nitrile, respectively, are illustrated in Scheme 1. Both incorporate the primary one-electron oxidation of **3b** at $E_1°$ to the co-ordinatively unsaturated 31-electron system $[Ru_2(CO)_4(\mu\text{-etipdp})_2]^+$ being followed by the spontaneous uptake of a nitrile molecule to give $[Ru_2(\mu\text{-}CO)\text{-}$



Scheme 1 Possible pathways for the electrochemical oxidation of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ in organonitrile solvents

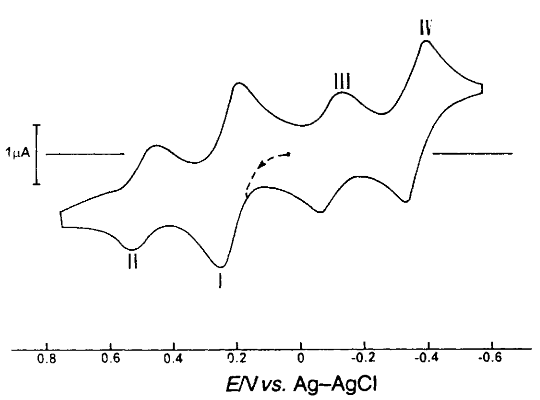


Fig. 3 Cyclic voltammogram of $[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2]$-$[tcnq]$ (0.1 mmol dm^{-3}) measured in CH_2Cl_2. Conditions as in Fig. 1

$(CO)_3(RCN)(\mu\text{-etipdp})_2]^+$ of possible structure shown; the structure suggested for the latter is on the basis that a number of other diphosphorus ligand-bridged diruthenium compounds have been established to adopt related structures, *e.g.* $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-etmdp})_2]$,[1] $[Ru_2(\mu\text{-}I)I(CO)_3(\mu\text{-etipdp})_2]$[4] and $[Ru_2(\mu\text{-}\eta^1\text{-}CCHMe)(CO)_4(\mu\text{-etipdp})_2]$.[14] It is envisaged that $[Ru_2(\mu\text{-}CO)(CO)_3(RCN)(\mu\text{-etipdp})_2]^+$ could react further *via* one of two pathways. Pathway (*a*) involves the one-electron oxidation of this monocationic species to the 32-electron dication $[Ru_2(\mu\text{-}CO)(CO)_3(RCN)(\mu\text{-etipdp})_2]^{2+}$ followed by the uptake of a second nitrile molecule to give $[Ru_2(CO)_4(RCN)_2(\mu\text{-etipdp})_2]^{2+}$, while the alternative pathway, (*b*), involves the uptake of a nitrile ligand by the still co-ordinatively unsaturated system $[Ru_2(\mu\text{-}CO)(CO)_3(RCN)(\mu\text{-etipdp})_2]^+$ to produce the 35-electron monocation $[Ru_2(CO)_4(RCN)_2(\mu\text{-etipdp})_2]^+$ followed by a one-electron oxidation to afford the final product. However, on the basis that $[Ru_2(CO)_4(RCN)_2(\mu\text{-etipdp})_2]^+$ (R = Me or Ph) will be more electron-rich than $[Ru_2(\mu\text{-}CO)(CO)_3(RCN)(\mu\text{-etipdp})_2]^+$, oxidation of the former should occur more readily than that for the latter, *i.e.* $E_3°$ should be more cathodic than $E_2°$, both of which will of course be more cathodic than $E_1°$.

(*ii*) **$[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2][tcnq]$.** The cyclic voltammogram of $[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2][tcnq]$ has been measured in CH_2Cl_2 and is illustrated in Fig. 3. The primary anodic wave (I) has an $E_{\frac{1}{2}}$ value of +0.22 V and corresponds to the one-electron oxidation of non-co-ordinated tcnq$^-$. A second anodic wave, II, is observed at $E_{\frac{1}{2}}$ = +0.49 V, assigned to the one-electron oxidation of co-ordinated tcnq$^-$. Two cathodic waves, III and IV, at $E_{\frac{1}{2}}$ = 0.12 and −0.36 V respectively, are observed in the reverse scan and correspond to the one-electron reduction of co-ordinated and free tcnq$^-$, respectively. Significantly the peak heights for the waves corresponding to unco-ordinated tcnq are greater than those for the corresponding waves for co-ordinated tcnq, this pattern also being observed for $[Ru_2(\eta^1\text{-tcnq})(CO)_5\{\mu\text{-}(RO)_2PNEtP(OR)_2\}_2][tcnq]$ (R = Me or Pr^i).[7] This is readily explained in terms of the free tcnq having a larger diffusion coefficient than that of the bulky cation.

Crystal structure of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][BF_4]_2\cdot CH_2Cl_2$

The structure of the cation of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][BF_4]_2\cdot CH_2Cl_2$ has been determined X-ray crystallographically and is illustrated in Fig. 4. Selected interatomic distances and angles are given in Table 1. The two ruthenium atoms, each of which is approximately octahedral, are linked through two bridging tetraisopropoxydiphosphazane ligands *trans* disposed with respect to each other, and by a formal ruthenium–ruthenium bond [2.878(2) Å], marginally shorter than that [2.890(3) Å] for $[Ru_2(CO)_5(PhCN)(\mu\text{-etipdp})_2][PF_6]_2$.[6] The co-ordination around each ruthenium atom is completed by two carbonyl groups and an acetonitrile ligand, with the two acetonitriles being co-ordinated *trans* with respect to each other in equatorial positions. The cation adopts an essentially staggered conformation as reflected by P(1)–Ru(1)–Ru(2)–P(4) and P(2)–Ru(2)–Ru(1)–P(3) torsion angles of 22.1 and 27.6° respectively; very similar staggering was observed for the pentacarbonyl species $[Ru_2(CO)_5(PhCN)(\mu\text{-etipdp})_2]^{2+}$ with corresponding torsion angles of 28.4 and 31.0° respectively.[6] Remaining interatomic distances and angles show no unusual features.

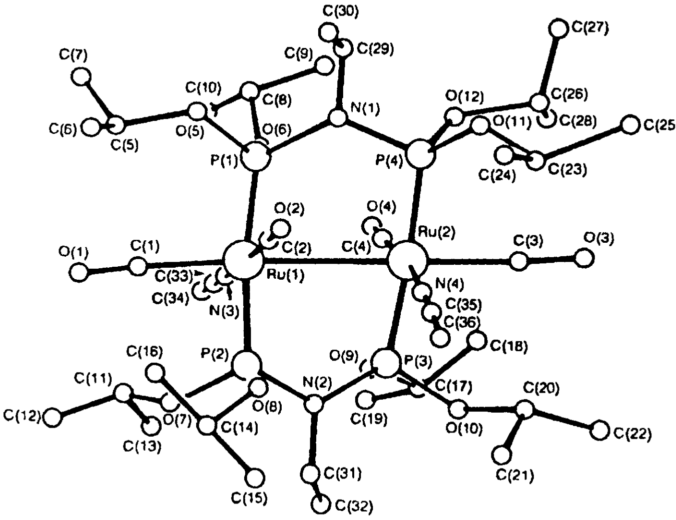


Fig. 4 Structure of the cation in $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][BF_4]_2\cdot CH_2Cl_2$ showing the atom labelling scheme

Experimental

The unsaturated species $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ was synthesised according to a previously described procedure.[1] All reactions and manipulations were carried out under an atmosphere of argon using Schlenk techniques. The nitrile solvents were purified and dried by refluxing over P_2O_5, followed by at least two fractional distillations through a 1 m glass-helice vacuum-jacketed column [at 10 mmHg (*ca.* 1333 Pa) for benzonitrile and at atmospheric pressure for acetonitrile]. Electrochemical procedures and instrumentation used were the same as those described previously.[3] Electrochemical data are summarised in Table 2. Potentials are quoted relative to a pseudo-Ag–AgCl reference electrode the potential of which was standardised against the ferrocene–ferrocenium couple for each experiment. Potentials for the latter *versus* the Ag–AgCl electrode in the different solvents (all 0.1 mol dm^{-3} in NBu_4PF_6 were 0.435 (MeCN), 0.405 (PhCN) and 0.425 V (CH_2Cl_2). Infrared spectra were measured on a Perkin-Elmer 457 spectrometer, $^{31}P\text{-}\{^1H\}$ NMR spectra on a Varian FT 80A instrument, and ^1H NMR spectra on a Varian Gemini 200 spectrometer. Relevant spectroscopic data are summarised in Table 3.

Table 1 Selected interatomic distances (Å) and angles (°) for $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][BF_4]_2\cdot CH_2Cl_2$

Ru(1)–Ru(2)	2.878(2)	Ru(1)–P(1)	2.340(3)
Ru(1)–P(2)	2.345(3)	Ru(1)–N(3)	2.094(10)
Ru(2)–P(3)	2.344(3)	Ru(2)–P(4)	2.349(3)
Ru(2)–N(4)	2.098(8)	N(3)–C(33)	1.14(2)
N(4)–C(35)	1.12(1)	C(33)–C(34)	1.44(2)
C(35)–C(36)	1.51(2)		
Ru(2)–Ru(1)–P(1)	86.1(1)	Ru(2)–Ru(1)–P(2)	87.1(1)
Ru(2)–Ru(1)–N(3)	91.7(3)	Ru(2)–Ru(1)–C(1)	172.0(3)
Ru(2)–Ru(1)–C(2)	84.3(4)	P(1)–Ru(1)–P(2)	173.0(1)
P(1)–Ru(1)–N(3)	91.8(3)	P(1)–Ru(1)–C(1)	100.0(4)
P(1)–Ru(1)–C(2)	86.6(4)	P(2)–Ru(1)–N(3)	89.3(3)
P(2)–Ru(1)–C(1)	86.8(4)	P(2)–Ru(1)–C(2)	91.8(4)
N(3)–Ru(1)–C(1)	93.3(4)	N(3)–Ru(1)–C(2)	175.7(5)
C(11)–Ru(1)–C(2)	90.9(5)	Ru(1)–Ru(2)–P(3)	87.5(1)
Ru(1)–Ru(2)–P(4)	90.1(1)	Ru(1)–Ru(2)–N(4)	88.2(2)
Ru(1)–Ru(2)–C(3)	178.0(4)	Ru(1)–Ru(2)–C(4)	86.3(4)
P(3)–Ru(2)–P(4)	174.8(1)	P(3)–Ru(2)–N(4)	89.2(4)
P(3)–Ru(2)–C(3)	92.3(4)	P(3)–Ru(2)–C(4)	89.0(4)
P(4)–Ru(2)–N(4)	95.4(3)	P(4)–Ru(2)–C(3)	89.9(4)
P(4)–Ru(2)–C(4)	86.2(4)	N(4)–Ru(2)–C(3)	93.7(5)
N(4)–Ru(2)–C(4)	174.3(4)	C(3)–Ru(2)–C(4)	91.7(5)
Ru(1)–N(3)–C(33)	178.0(10)	N(3)–C(33)–C(34)	178.4(14)
Ru(2)–N(4)–C(35)	177.8(9)	N(4)–C(35)–C(36)	178.3(13)

Table 2 Electrochemical data

Compound	Solvent	Redox step*	E_{pa}/V	E_{pc}/V	$E_{\frac{1}{2}}$/V
$[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$	MeCN	1. Ox.	0.04		
		2. Ox.	1.67	1.59	1.63
		X		−1.40	
	PhCN	1. Ox.	0.05		
		2. Ox.	1.68	1.57	1.63
		X		−1.28	
$[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-etipdp})_2]$	PhCN	1. Ox.	−0.08	−0.17	−0.13
		2. Ox.	0.24		
		X		−1.27	
$[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$	MeCN	1. Red.		−1.45	
		Y	0.02		
		Z	1.72	1.55	1.64
$[Ru_2(CO)_4(PhCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$	PhCN	1. Red.		−1.30	
		Y	0.06		
		Z	1.70	1.58	1.64
$[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2][tcnq]$	CH_2Cl_2	1. Ox.	0.26	0.19	0.22
		2. Ox.	0.53	0.45	0.49
		1. Red.	−0.08	−0.15	−0.12
		2. Red.	−0.33	−0.38	−0.36

* Ox. = Oxidation, Red. = reduction.

Table 3 Infrared and $^{31}P-\{^1H\}$ NMR spectroscopic data

Compound	$\tilde{\nu}(CO)$[a]/cm^{-1}	$^{31}P-\{^1H\}$ NMR[b]
$[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$[c]	2050 (sh), 2030s, 2001s	134.5 (s)
$[Ru_2(CO)_4(PhCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$[d]	2045 (sh), 2027s, 1987s	131.8 (s)
$[Ru_2(CO)_5(MeCN)(\mu\text{-etipdp})_2][SbF_6]_2$	2094w, 2053s, 2031s, 2003m	130.0 (AA'BB')
$[Ru_2\{\mu\text{-OC(Me)O}\}(CO)_4(\mu\text{-etipdp})_2]PF_6$	2030s, 2001vs, 1972s, 1947m,[e] 1550 (acetate)	135.6 (s)[f]
$[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2][tcnq]$[g]	2023s, 1981s (br)	
$[Ru_2(\mu\text{-Cl})(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]_2$	2034s, 2002vs, 1975s, 1951ms, 1520 (*p*-chloranil)	130.9 (s)[f]

[a] Measured in CH_2Cl_2, unless otherwise stated. Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] δ In ppm relative to H_3PO_4; measured at room temperature in $(CD_3)_2CO$ unless otherwise stated. Abbreviations: s = singlet, AA'BB' = centre of an AA'BB' pattern of peaks. [c] ν(CN): 2298w cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, reference $SiMe_4$]: δ 2.70 (s, 6 H). [d] ν(CN): 2265w cm^{-1}. ^{1}H NMR: δ 7.74–8.02 (m, 10 H). [e] Measured in $CHCl_3$. [f] Measured in $CDCl_3$. [g] ν(CN): 2189vs and 2146ms cm^{-1}. For $[Ru_2(\eta^1\text{-tcnq})(CO)_5(\mu\text{-etipdp})_2][tcnq]$: ν(CO) ($CH_2Cl_2$) 2050s, 2030s and 1990m cm^{-1}.

Table 4 Non-hydrogen atomic coordinates (× 10^4) for $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][BF_4]_2\cdot CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	1 908(1)	9 798(1)	8 203(1)	C(15)	1 938(19)	7 356(11)	9 722(8)
Ru(2)	3 054(1)	10 739(1)	8 908(1)	C(16)	654(14)	7 715(14)	9 054(11)
P(1)	1 249(2)	10 960(2)	7 897(1)	C(17)	5 931(9)	10 062(9)	8 455(7)
P(2)	2 663(2)	8 724(2)	8 590(1)	C(18)	6 012(12)	10 892(10)	8 562(8)
P(3)	4 186(2)	9 748(2)	8 890(1)	C(19)	6 390(14)	9 745(15)	7 391(9)
P(4)	1 942(2)	11 744(2)	8 841(1)	C(20)	4 633(8)	9 851(8)	9 979(5)
O(1)	610(7)	8 619(5)	7 652(4)	C(21)	4 287(11)	9 125(8)	10 253(5)
O(2)	447(6)	9 854(6)	9 084(4)	C(22)	5 499(11)	10 163(10)	10 227(6)
O(3)	4 302(8)	11 793(6)	9 592(4)	C(23)	1 575(11)	11 839(8)	9 934(6)
O(4)	3 948(6)	11 394(5)	7 903(4)	C(24)	623(12)	11 481(10)	10 111(7)
O(5)	221(6)	10 981(5)	7 650(3)	C(25)	1 804(14)	12 584(8)	10 252(6)
O(6)	1 930(6)	11 341(4)	7 445(3)	C(26)	2 896(12)	13 118(7)	8 879(6)
O(7)	2 708(6)	7 973(4)	8 217(3)	C(27)	2 243(13)	13 838(9)	8 859(9)
O(8)	2 131(6)	8 389(4)	9 105(3)	C(28)	3 801(11)	13 292(10)	8 593(7)
O(9)	4 955(6)	9 851(5)	8 418(3)	C(29)	276(10)	12 202(8)	8 390(6)
O(10)	4 869(5)	9 673(5)	9 408(3)	C(30)	−594(10)	11 943(11)	8 697(6)
O(11)	1 426(6)	12 051(5)	9 374(3)	C(31)	4 313(9)	8 141(6)	8 984(6)
O(12)	2 392(6)	12 506(4)	8 596(3)	C(32)	5 305(9)	8 074(8)	8 806(6)
N(1)	1 040(7)	11 611(5)	8 416(4)	C(33)	3 497(8)	9 846(7)	7 255(5)
N(2)	3 776(7)	8 841(5)	8 800(4)	C(34)	4 176(11)	9 898(11)	6 822(6)
N(3)	2 947(7)	9 821(5)	7 596(4)	C(35)	2 068(8)	9 884(6)	9 918(4)
N(4)	2 400(6)	10 194(5)	9 570(3)	C(36)	1 591(13)	9 468(9)	10 381(5)
C(1)	1 117(9)	9 063(7)	7 810(5)	F(1)	4 339(8)	15 196(7)	9 076(4)
C(2)	1 024(9)	9 842(7)	8 768(5)	F(2)	3 089(14)	15 997(10)	9 041(7)
C(3)	3 842(9)	11 381(7)	9 358(6)	F(3)	4 462(12)	16 375(10)	9 392(7)
C(4)	3 590(8)	11 143(7)	8 278(5)	F(4)	4 396(16)	16 214(13)	8 565(9)
C(5)	−166(9)	10 403(8)	7 268(5)	B(1)	3 868(34)	15 950(25)	8 856(19)
C(6)	−974(10)	9 986(10)	7 586(8)	F(5)	−1 720(9)	13 994(7)	9 329(5)
C(7)	−483(12)	10 794(10)	6 755(6)	F(6)	−2 405(10)	13 625(8)	8 550(6)
C(8)	1 697(11)	11 962(8)	7 065(5)	F(7)	−1 862(11)	14 863(9)	8 669(6)
C(9)	2 068(16)	12 728(8)	7 262(6)	F(8)	−865(14)	13 966(10)	8 637(7)
C(10)	2 164(16)	12 721(11)	6 521(6)	B(2)	−1 836(19)	14 133(14)	8 786(10)
C(11)	2 896(9)	7 906(7)	7 647(5)	C(37)	1 709(16)	4 558(10)	5 331(7)
C(12)	2 446(12)	7 195(9)	7 467(7)	Cl(1)	1 906(5)	5 473(3)	5 471(3)
C(13)	3 975(13)	7 890(10)	7 545(8)	Cl(2)	1 894(6)	3 933(4)	5 865(3)
C(14)	1 689(13)	7 633(8)	9 185(7)				

Syntheses

$[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2]X_2$ (X = BF_4, PF_6 or SbF_6). Two molar equivalents of $AgBF_4$ (0.08 g, 0.40 mmol), $AgPF_6$ (0.10 g, 0.40 mmol) or $AgSbF_6$ (0.14 g, 0.40 mmol) in acetonitrile (2 cm^3) were added dropwise to $[Ru_2(\mu_{sb}\text{-CO})_2(CO)_2(\mu\text{-etipdp})_2]$ (0.20 g, 0.20 mmol) in acetonitrile (10 cm^3) and the resultant solution stirred for 2 h during which time silver metal separated. The pale yellow solution was filtered through a glass-fibre frit and the volume of the filtrate concentrated under reduced pressure to *ca.* 2 cm^3. Addition of toluene (*ca.* 2 cm^3) resulted in the separation of a white crystalline material which was recrystallised from CH_2Cl_2–Et_2O. Yields: BF_4 salt, 0.18 (70); PF_6 salt, 0.19 (70); SbF_6 salt, 0.22 g (70%) (Found: C, 33.4; H, 5.4; N, 4.0. Calc. for $C_{36}H_{72}B_2F_8N_4O_{12}P_4Ru_2$: C, 33.2; H, 5.6; N, 4.2. Found: C, 31.8; H, 5.2; N, 4.1. Calc. for $C_{36}H_{72}F_{12}N_4O_{12}P_6Ru_2$: C, 31.6; H, 5.3; N, 4.1. Found: C, 27.8; H, 4.9; N, 3.6. Calc. for $C_{36}H_{72}F_{12}N_4O_{12}P_4Ru_2Sb_2$: C, 27.9; H, 4.7; N, 3.6%).

$[Ru_2(CO)_4(PhCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$. This compound was synthesised by treatment of $[Ru_2(\mu_{sb}\text{-CO})_2(CO)_2(\mu\text{-etipdp})_2]$ (0.20 g, 0.20 mmol) with $AgSbF_6$ (0.14 g, 0.40 mmol) in benzonitrile (2 cm^3) according to the procedure described above and recrystallised from CH_2Cl_2–Et_2O. Yield: 0.23 g (70%) (Found: C, 33.3; H, 4.3; N, 3.6. Calc. for $C_{46}H_{60}F_{12}N_4O_{12}P_4Ru_2Sb_2$: C, 33.0; H, 4.6; N, 3.4%).

$[Ru_2(\eta^1\text{-tcnq})(CO)_4(thf)(\mu\text{-etipdp})_2][tcnq]$. A solution of $[Ru_2(\mu_{sb}\text{-CO})_2(CO)_2(\mu\text{-etipdp})_2]$ (0.10 g, 0.10 mmol) in thf (2 cm^3) was added dropwise to a stirred solution of two molar equivalents of tcnq (0.04 g, 0.20 mmol) in thf (3 cm^3). The intense green solution was concentrated under reduced pressure to *ca.* 2 cm^3 and diethyl ether added to precipitate the product. The green residue was washed with diethyl ether and dried thoroughly. Yield: 0.21 g (60%) (Found: C, 38.9; H, 5.5; N, 5.7. Calc. for $C_{60}H_{82}N_{10}O_{13}P_4Ru_2$: C, 39.0; H, 5.3; N, 5.7%).

Reaction of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ with *p*-chloranil

Two molar equivalents of *p*-chloranil (0.10 g, 0.40 mmol) in toluene (3 cm^3) were added dropwise to a stirred solution of $[Ru_2(\mu_{sb}\text{-}CO)_2(CO)_2(\mu\text{-etipdp})_2]$ (0.20 g, 0.20 mmol) in toluene (5 cm^3). The resultant yellow-brown material which separated was isolated and washed with diethyl ether. The product was purified by crystallisation from thf–diethyl ether and characterised as $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]_2$. Yield: 0.21 g (65%) (Found: C, 35.4; H, 4.7; Cl, 20.8; N, 1.7; P, 7.7. Calc. for $C_{44}H_{66}Cl_9N_2O_{16}P_4Ru_2$: C, 34.7; H, 4.4; Cl, 20.9; N, 1.8; P, 8.1%).

An excess of $NaBPh_4$ (0.05 g, 0.15 mmol) in acetone (3 cm^3) was added to a stirred solution of $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2][p\text{-}OC_6Cl_4O]_2$ (0.14 g, 0.10 mmol) in acetone (5 cm^3) at room temperature. The resultant green precipitate of sodium tetrachlorocatecholate was filtered off, the filtrate evaporated to dryness under reduced pressure and the residue crystallised from CH_2Cl_2–diethyl ether to afford $[Ru_2(\mu\text{-}Cl)(CO)_4(\mu\text{-etipdp})_2]BPh_4$. Yield: 0.19 g (85%) (Found: C, 49.7; H, 5.9; Cl 2.8; N, 1.6; P, 8.6. Calc. for $C_{56}H_{86}BClN_2O_{12}P_4Ru_2$: C, 49.8; H, 6.4; Cl, 2.6; N, 2.0; P, 9.1%).

Reactions of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$

With carbon monoxide. A stream of CO was passed slowly through a solution of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$ (0.10 g, 0.07 mmol) in acetone (10 cm^3) under reflux for 5 h. The solvent was removed under reduced pressure and the product identified as $[Ru_2(CO)_5(MeCN)(\mu\text{-etipdp})_2][SbF_6]_2$ by spectroscopic means.

With acetate ions. Two molar equivalents of solid AgO_2CMe (0.04 g, 0.22 mmol) were added to a solution of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][SbF_6]_2$ (0.15 g, 0.11 mmol) in acetone (7 cm^3) and stirred for 12 h. The pale yellow solution was filtered and the solvent removed under reduced pressure. The yellow residue was extracted with chloroform, the resultant solution filtered and the filtrate evaporated to dryness to afford a pale yellow microcrystalline product identified spectroscopically as $[Ru_2\{\mu\text{-}OC(Me)O\}(CO)_4(\mu\text{-etipdp})_2]SbF_6$.

Structure determination of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-etipdp})_2][BF_4]_2\cdot CH_2Cl_2$

Crystal data. $C_{37}H_{72}B_2Cl_2F_8N_4O_{12}P_4Ru_2$, $M_r = 1336.9$, orthorhombic, space group $P2_12_12_1$, $a = 14.099(1)$, $b = 17.317(2)$, $c = 24.659(6)$ Å, $U = 6020.5(4)$ Å^3, $Z = 4$, $D_c = 1.474$ g cm^{-3}, μ(Mo-Kα) = 7.66 cm^{-1}, $F(000) = 2728$, $T = 295$ K, crystal dimensions 0.39 × 0.19 × 0.15 mm.

4657 Data were collected on a CAD4 diffractometer by the variable-speed ω–2θ scan method in the range $3 \leqslant 2\theta \leqslant 46°$ with Mo-Kα radiation ($\lambda = 0.710\,69$ Å); 4284 were unique of which 3848 were observed $[I \geqslant 3\sigma(I)]$ and these were used for the refinement of the structure. The data were corrected for absorption by the ψ-scan method[15] with maximum and minimum transmission factors of 0.999 and 0.887. The structure was solved by standard Patterson methods and subsequently completed by Fourier recycling and refinement.[16] Non-hydrogen atoms were anisotropic except for the fluorine atoms which were assigned isotropic thermal factors because of rotational disorder associated with the tetrafluoroborate anions. (Close examination of the difference electron-density map did not reveal a workable disorder model for the anions.) Hydrogen atoms were placed in calculated positions and refined with a common isotropic thermal factor. The final refinement (on F) converged at $R = 0.048$ and $R' = 0.049$ using the weighting scheme $w = 1/[\sigma^2(F_o) + 0.0005(F_o)^2]$ (470 parameters, maximum shift/error = 0.22, maximum difference peak = 0.83 e Å^{-3}). Inversion of all the atom coordinates and re-refinement of the structure gave slightly higher R factors. Neutral atom scattering factors were used with corrections for anomalous dispersion.[17] Final atomic fractional coordinates are listed in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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