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A REVIEW OF PLATINUM METAL NITRATO COMPLEXES

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CONTENTS

A. INTRODUCTION

Notwithstanding the considerable advance in transition metal nitrate chemistry in the 1960s [1] the great majority of platinum metal nitrato complexes that had been identified towards the end of the decade were largely of the 'classical' type in which nitrate, as a relatively hard Lewis base, tended to follow the convention rationalised by Pearson [2], that ligands of this type would complex with these metals in high oxidation states. Furthermore, nitrate tended to be associated in the same coordination sphere with similar bases of low polarity and minimal π-bonding, following the rule of Jorgensen [3] that similar ligand types tend to cohabit in the same coordination sphere. Thus, with the exception of a small number of platinum and palladium tertiary phosphine complexes and the special case of ruthenium bound to nitrosyl [4], the nitrate ligand was found almost exclusively with bound water, hydroxide, nitrite, halide, ammonia or amines.

In recent years, however, a number of platinum metal nitrato complexes have been synthesised in which the central metal atom holds a low oxidation state which appears to be stabilised by the presence of ligands such as phosphines, carbonyl or hydride, and many of these complexes show a surprisingly high thermal and kinetic stability. In many cases the degree of coordination has been determined from IR data, though conductivity measurements have also been extensively used. Infrared has additionally been applied to the determination of mode of nitrate coordination, though some doubt has been cast on this approach [5,6]. A more precise determination from Raman spectroscopy has been attempted for a number of the compounds, but their generally intense colour has until recently prevented meaningful data from being obtained [7,8a].

Various electronic effects of the nitrate group bound to the platinum metals have been studied, especially in the complexes of platinum itself. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR has been applied, and interpretations have been obtained both from relative chemical shifts and from the magnitude of platinum—fluorine and platinum—phosphorus coupling constants, and from IR [ν(M—C) and ν(C—O)] data. Comparison with other anionic ligands have been made in order to establish series of *trans* influence, *cis* influence, and degree of metal—ligand π-bonding.

The leaving group property of nitrate from platinum metals has been most extensively studied by conductivity measurements and pK_a determinations of hydrolysis reactions, though the relative ability of the ligand to enhance metallation and hydrocarbon insertion reactions has also provided a qualitative indication of its leaving group tendency. A number of platinum metal nitrato complexes have been found to possess catalytic activity.

This review is confined to platinum metal complexes in which the nitrate ligand shows evidence of coordination to the metal. It is not concerned with the wealth of compounds in which nitrate simply functions as the counter ion.

B. THE NITRATE LIGAND

Before embarking upon a detailed survey of nitrato complexes of the platinum metals in particular, a brief summary of the nitrate anion as a ligand is appropriate.

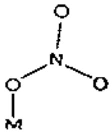
(a) Metal-nitrate covalency. Until the late 1950s, knowledge of metal nitrates was confined largely to their aqueous chemistry, in which the metal—nitrate bond was considered to be highly ionic. The majority of transition metal nitrates were commonly known to exist only as hydrates, and there was some doubt about the stable existence of many of these compounds in the anhydrous state.

However, following their studies on the preparation and properties of anhydrous copper nitrate, Addison and Hathaway were able to conclude [9] that, "in anhydrous compounds the nitrate group is capable of a type of bonding not hitherto realised". Evidence for covalency in this and many other metal-nitrate bonded systems has been furnished principally by the following. (i) IR and Raman data. Differences result from the lowering of symmetry of the

ion and the changes in bond order following coordination (see later).
(ii) UV absorption data. A move to higher frequency is observed for the weak absorption found at 33000 cm^{-1} [10] in the free ion. The preferred assignment of this transition is ($\pi^* \leftarrow n$) [9]. Since the other strong absorption frequency of the nitrate ion at 50000 cm^{-1}, assigned ($\pi^* \leftarrow \pi$), is not greatly changed, it is most likely that the move to higher energy of the forbidden transition is caused by a lowering in energy of the nonbonding orbitals of the nitrate ion, brought about by coordination [10].
(iii) Solution chemistry. Solutions of many transition metal nitrato complexes have been shown to exhibit negligible conductivity, confirmed by colligative molecular weight determinations which show little dissociation [11—13].
(iv) Structural determinations. X-ray crystallographic studies have shown the nitrate group to influence the overall stereochemistry in the same manner as any other covalently bound ligand [14]. Furthermore, the oxygen—nitrogen bonds of bound nitrate have been shown to be distorted relative to the O—N dimensions of the free ion [15]. This has been attributed to polarisation of the ion through covalent interaction with the metal [16].

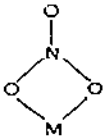
(b) Modes of coordination. The nitrate ion is known to coordinate as a unidentate, bidentate or bridging ligand [1]. A detailed survey of the structures of the ligand in these modes is to be found in ref. 17.

Unidentate coordination is relatively uncommon, being found only when the number of metal—nitrate bonds that can be formed is limited to one [17]. Such a situation is met in aqueous chemistry, when water successfully competes for the second coordination site [18,19]. As a unidentate ligand, nitrate appears to favour bent (C_s) symmetry (I), with the M—O—N angle within the region 110—120° [17].



(I)

The bidentate mode of coordination is most common. The bidentate nitrato group exists generally as the symmetrically bound ligand (C_{2v}) (II), though an appreciably unsymmetrical form is also known [20], in which the distortion is found principally in the non-equivalence of the two M—O bonds, the N—O bond lengths remaining similar.



(II)

Examples of bridging through two and through only one oxygen atom of the nitrate ligand have been reported [21—23], although this mode of coordination is rare.

(c) Position in the spectrochemical series. The nitrate ligand is placed between water and DMSO, low in the spectrochemical series [26]. Consequently nitrato complexes are usually found in the high spin state.

(d) IR and Raman activity. Free nitrate ion belongs to the D_{3h} point group. On coordination the threefold axis of rotation is lost and the coordinated nitrate ligand now belongs to the C_{2v} point group (bidentate) or the C_s point group (unidentate). In either case the degeneracy of both the NO_2 stretching (ν_3) and NO_2 bending (ν_4) frequencies is lifted to give six fundamental vibrations.

The determination of denticity of coordinated nitrate from IR and Raman data has been the subject of much discussion [24,25]. The following methods of determining denticity from vibrational spectra have been proposed.

(i) Calculation has shown [25] that, as for carbonate, separation between the two highest nitrate absorptions (attributed to $\nu(NO_2)$) is a function mainly of ligand polarisation. For a given degree of polarisation the $\nu(NO_2)$ symmetric and asymmetric separation is found to be greater for bidentate coordination. However, the difference between separations for the two modes is small, and for this reason the denticity of nitrate in an isolated complex cannot reliably be predicted by this method [6,27].

(ii) Topping [6] has suggested that nitrate, like coordinated carbonate, might exhibit two bands for bidentate coordination (attributable to $\nu(MO_2)_{sym}$ and $\nu(MO_2)_{asym}$) and one for unidentate coordination (attributable to $\nu(MO)$) in the far IR region. However, the validity of this approach has been questioned [28] both on theoretical and empirical grounds, and few literature examples of its application are to be found.

(iii) It has been shown [25] that on coordination in the bidentate mode, the symmetric NO_2 stretch of nitrate moves to higher frequency, whereas the asymmetric NO_2 stretch accounts for the higher frequency in the unidentate case. The former, possessing symmetry A_1, should be Raman polarised whilst the latter, of B_1 symmetry, should exhibit Raman depolarisation. Reported applications of this method are relatively uncommon, possibly as a consequence of the low intensity of the Raman bands of the often intensely coloured transition metal nitrato complexes [7,29]. However, where the approach has been applied anomalies were not apparent.

(iv) Comparison of the Raman intensities of the three highest frequency absorptions attributable to nitrate shows [17] that for unidentate coordination the second highest band is relatively intense, whereas for bidentate coordination this middle band is invariably the weakest. Although this method has been successfully applied to simple nitrato complexes, the generally low intensities of all bands together with the presence of other absorptions may explain the absence of its application to mixed nitrato complexes.

(v) It has been established that infrared combination bands at ca. 1750 cm^{-1} may be used to distinguish between various modes of coordination of nitrate groups. The magnitude of the splitting of these bands is generally larger for bidentate than for unidentate coordination [30]. The vibrational spectra of nitrates and nitrato complexes are surveyed annually in the Chemical Society Specialist Report series dealing with spectroscopic properties of inorganic and organometallic compounds.

C. METHODS OF PREPARATION

The classical synthetic procedures employed in transition metal nitrato chemistry [1,31] are available for the synthesis of platinum metal nitrato complexes. In addition several novel routes have been exploited.

Metathesis is most commonly employed, sometimes even when analogous complexes of other anionic ligands have been obtained by direct reaction with the corresponding acid. This choice probably reflects fears that nitric acid might oxidise other ligands, increase the oxidation state of the metal or oxidatively decompose the reactants. Typically, the halo-precursor is shaken with an acetone—water or alcohol—water solution of silver nitrate. In most cases the reaction occurs quickly and cleanly at ambient temperature, poor solubility of the silver halide helping to shift the equilibrium in favour of the required product [32]. However, alkali metal nitrates have also been successfully employed [33]. Various concentrations of nitric acid have been used to supply the nitrate ligand, without onset of unwanted oxidation. For example, $[IrCl(NO_3)_2(CO)(PPh_3)_2]$ has been obtained by the reaction of concentrated nitric acid with a tetrahydrofuran solution of $[IrCl(CO)(PPh_3)_2]$ at 313 K [34], and $[RuCl(NO_3)(CO)(PMe_2Ph)_3]$ by treating $[RuHCl(CO)(PMe_2Ph)_3]$ with dilute nitric acid at ambient temperature [35].

The reaction of solid dinitrogen pentoxide with iridium(III) bromide affords a polynuclear nitrate [29]. The nitrate ligand has additionally been obtained when lower oxides of nitrogen react with oxygenated precursors. The species $[M(NO_3)_2(PPh_3)_2]$ (M = Pt or Pd) have been prepared by treating the dioxygen addition compounds $[MO_2(PPh_3)_2]$ with nitrogen dioxide/dinitrogen tetroxide [36,37]; the addition of nitrogen monoxide to ruthenium tetroxide affords a polynuclear nitrate [38].

Oxidation of the nitrosyl ligand has provided another synthetic route to nitrato complexes as, for example, when a benzene solution of $[IrClX(NO)(CO)(PPh_3)_2]$ (X = anionic ligand) is stirred in a stream of dioxygen at ambient temperature to yield $[IrClX(NO_3)(CO)(PPh_3)_2]$ (ref. 39).

A number of platinum metal nitrato derivatives, especially those of palladium, have been prepared by substituting other ligands into the simple metal nitrate. Thus, for example, $[Pd(NO_3)_2(PBu^t{}_2H)_2]$ has been isolated from mixed methanol solutions of palladium(II) nitrate and the free phosphine [40].

(i) Ruthenium

All known nitrato complexes of ruthenium contain the metal in the formal +2 oxidation state.

Nitrosyl complexes. Ruthenium nitrate chemistry is dominated by the exceptionally strong affinity of ruthenium(II) for the nitrosyl ligand [4]. Indeed ruthenium in other oxidation states has been found to react with nitric acid to yield ruthenium(II) nitrosyl complexes as the only identifiable products [42]. IR nitrosyl absorption frequencies for all these compounds are found close to 1935 cm^{-1}, suggesting the higher N—O bond order associated with linear Ru—N—O moieties [4]. Nearly all nitrato complexes of ruthenium may therefore be thought of as derivatives of "$Ru(NO)^+$" (ref. 4). The majority of such complexes contain, in addition to nitrate, a variety of oxygen or nitrogen donor ligands (OH^-, H_2O, NO_2^-), and are orange-brown products with high water solubility. The early work in this field was performed by Jolly [161]. More recently, extensive studies on the ruthenium (II) nitrate system have been prompted by the use of nitric acid solutions in the extraction of ruthenium isotopes from uranium and plutonium fission products in the nuclear power industry [41—48, 162—179].

Aqueous solutions containing a wide variety of ruthenium(II) nitrato complexes have been generated by treatment of "$[Ru(NO)(OH)_3]_n$" (refs. 41, 162, 163) or $M_2[Ru(NO)(NO_2)_4(OH)]$ (refs. 41, 162) with nitric acid, and by the treatment of RuO_4 with nitrogen monoxide in nitric acid solution [41]. Species present in these solutions appear to belong primarily to three series of ruthenium(II) nitrosyl complexes [41,162,163]

$$[Ru(NO)(NO_3)_x(H_2O)_{5-x}]^{(3-x)+} \qquad (x = 1\text{—}5)$$

$$[Ru(NO)(NO_3)_y(OH)(H_2O)_{4-y}]^{(2-y)+} \qquad (y = 1\text{—}4)$$

$$[Ru(NO)(NO_3)(OH)_z(H_2O)_{4-z}]^{(2-z)+} \qquad (z = 1\text{—}4)$$

The numerous solvolysis,

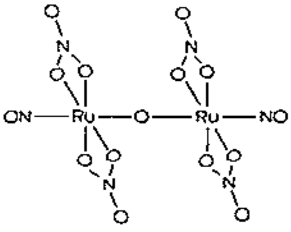
$$[Ru(NO)(NO_3)_x(H_2O)_y]^{(3-x)+} + H_2O \rightleftharpoons [Ru(NO)(NO_3)_{x-1}(H_2O)_{y+1}]^{(4-x)+} + NO_3^-$$

and hydrolysis,

$$[Ru(NO)(NO_3)_x(H_2O)_y]^{(3-x)+} \rightleftharpoons [Ru(NO)(NO_3)_x(OH)(H_2O)_{y-1}]^{(2-x)+} + H^+ \text{ aq.}$$

equilibria existing between the various nitrato complexes in aqueous nitric acid solution have been studied [165], and repeated attempts have been made to identify, estimate and isolate the species present in solution using paper chromatography [44,162], solvent extraction [44,163,164,166], ion exchange [44,162,164] and spectroscopic [48] techniques. Products isolated from these solutions include the neutral complex $[Ru(NO)(NO_3)_3(H_2O)_2]$ [45] and the salt $K[Ru(NO)(NO_3)_4(H_2O)]$ [45]. Failure to isolate the corresponding pentanitrato salt $K_2[Ru(NO)(NO_3)_5]$ has been attributed to the high *trans* labilising power of the nitrosyl ligand [44]. However, Russian workers have treated $[Ru(NO)(NO_3)_3(H_2O)_2]$ with tri-octylammonium nitrate in the presence of nitric acid (to prevent the amine from entering the coordination sphere), and have isolated a cherry red complex which was assigned a structure "intermediate between $[(n\text{-}C_8H_{17})_3NH]_2^+[Ru(NO)(NO_3)_5]^{2-}$ and $[(n\text{-}C_8H_{17})_3NHNO_3]_2$-

$[Ru(NO)(NO_3)_3]$" (ref. 43). The use of tertiary amines and tri-*n*-butyl phosphate as extractants has been widely studied [43,163,166,169,174—177], and the complex $[Ru(NO)(NO_3)_3(^nBu_3PO_4)_2]$ has been isolated [45]. A related tributylphosphine oxide complex $[Ru(NO)(NO_3)_3(^nBu_3PO)_2]$ has also been reported [46]. Studies on the nitro/nitrato system $[Ru(NO)(NO_2)_{3-x}(NO_3)_x(H_2O)_2]$ ($x = 1$ or 2) have led to isolation of the complex $[Ru(NO)(NO_2)(NO_3)_2(H_2O)_2]$ (ref. 47). The reaction of dry nitrogen monoxide with ruthenium tetroxide in carbon tetrachloride affords a yellow-brown water soluble solid of empirical formula $RuN_3O_{7.5}$ (ref. 38). Various structures have been proposed [48], but the observed diamagnetism and infrared spectra favour a binuclear oxygen-bridged structure (III) with bidentate nitrate ligands [45,48]. Much additional work on the ruthenium(II)/nitrate systems is contained in conference abstracts [178] and in reports of the United Kingdom Atomic Energy Authority [179].



(III)

The dinitrosyl complex $[Ru(NO)_2(PPh_3)_2]$ has been shown to undergo oxidative addition with dioxygen to form $[Ru(NO)(NO_3)(O_2)(PPh_3)_2]$ (ref. 49a), probably via the highly reactive species $[Ru(NO)(NO_3)(PPh_3)_2]$. Conversion of $[RuCl(NO)(O_2)(PPh_3)_2]$ to $[RuCl(NO_3)(CO)_2(PPh_3)_2]$ by carbon monoxide provides a further example of the oxidation of bound nitrosyl to nitrate [49b].

The action of concentrated nitric acid on a benzene solution of $[RuH_2(CO)(PPh_3)_3]$ or $[RuH(OCOCH_3)(PPh_3)_3]$ afforded orange crystals of stoichiometry $[Ru(NO)(NO_3)_3(PPh_3)(OPPh_3)]$ (ref. 50).

Non-nitrosyl complexes. Ruthenium complexes containing nitrate in the absence of nitrosyl are rare; a result of the high tendency of ruthenium to abstract nitrosyl ligands from nitric acid and nitrates.

Dilute nitric acid with the hydride $[RuHCl(CO)(PMe_2Ph)_3]$ afforded $[RuCl(NO_3)(CO)(PMe_2Ph)_3]$ (ref. 35) accompanied by the evolution of dihydrogen. The white crystalline product was found to possess high thermal stability, though the complex was readily solvolysed by methanol at room temperature. Addition of excess nitric acid reprecipitated the product, suggesting the solvolysis to involve complete substitution of the nitrate. Further nitrate substitution of the chloride by metathesis with silver nitrate was unsuccessful.

Yellow crystals of $[Ru(NO_3)_2(CO)(PPh_3)_2]$ have been obtained by treatment of solid $[RuH_2(CO)(PPh_3)_3]$ with cold concentrated nitric acid [50]. Variable temperature ^{31}P NMR studies on the product show the phosphines to be mutually *cis*, and reveal rapid unidentate—bidentate intramolecular exchange between nitrate groups. Carbonylation of this product afforded the *cis* dicarbonyl [Ru$(NO_3)_2(CO)_2(PPh_3)_2$] (ref. 50) previously prepared by the action of carbon monoxide on [Ru(NO)$(NO_3)(O_2)(PPh_3)_2$] (ref. 49).

[Ru$(NO_3)_2(CO)(PPh_3)_2$] in refluxing alcohol has been found to yield white crystals of [RuH$(NO_3)(CO)(PPh_3)_2$] (ref. 50), probably via alcoholysis followed by β-elimination. Mild carbonylation of the latter complex yielded the *cis* dicarbonyl [RuH$(NO_3)(CO)_2(PPh_3)_2$] (ref. 50).

(ii) Osmium

The oxyosmyl salt $K_2[OsO_2(NO_2)_2(NO_3)_2]$ was prepared by direct substitution of the hydroxy groups in the complex anion $[OsO_2(OH)_4]^{2-}$ (ref. 51). Like its precursor, and the chloride $K_2[OsO_2Cl_4]$, the ion is thought to contain Os(IV) with the expected hexacoordinate geometry [8]. Lack of splitting of the nitrate IR absorptions has led to the suggestion that the two nitrate ligands are *trans* [51,52].

A number of osmium(II) nitrato complexes have been reported which are analogous both in preparation and properties to their ruthenium(II) counterparts [50] (see above): [Os$(NO_3)_2(CO)(PPh_3)_2$], [Os$(NO_3)_2(CO)_2(PPh_3)_2$], [OsH$(NO_3)(CO)(PPh_3)_2$] and [OsH$(NO_3)(CO)_2(PPh_3)_2$].

(iii) Rhodium

Rhodium(III). As might be expected, 'classical' nitrato complexes of rhodium contain the metal exclusively in its +3 oxidation state. A number of 'non-classical' rhodium(III) phosphine and related complexes are also known.

$K_3[Rh(NO_2)_6]$ is attacked by concentrated nitric acid to yield the complex anion $[Rh(NO_3)_6]^{3-}$ (ref. 53, 78).

Concentrated nitric acid will attack rhodium sesquioxide, Rh_2O_3, to form impure hydrated rhodium(III) nitrate, $Rh(NO_3)_3 \cdot 2\,H_2O$, as a red solid. [8b]. Pure $Rh(NO_3)_3$ has been obtained by treating RhI_3 with boiling concentrated nitric acid [78].

Treatment of the perchlorate salt of the complex ion $[Rh(NH_3)_5(OH_2)]^{3+}$ with nitric acid precipitated the nucleophilic substitution product $[Rh(NH_3)_5(NO_3)]^{2+}$, again as the perchlorate which, after repeated recrystallisation from nitric acid, yielded the analytically pure nitrate salt [54]. The latter has also been formed directly by a transfer of nitrate from outer to inner sphere by the action of heat on the nitrate salt of the precursor [8b].

The complex *mer*-$[Rh(NO_3)_3(NH_3)_3]$ has been reported to exhibit some cancer chemotherapeutic properties [55b].

Four pyridine nitrato derivatives have been reported: $[Rh(py)_4Br(NO_3)]^+$, $[Rh(py)_3(NO_3)_3]$, and *cis* and *trans* $[Rh(py)_2Cl_3(NO_3)]^-$ (py = pyridine) [1].

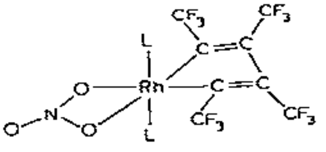
The hexacoordinate rhodium(III) complex $[RhBr_3(L)]$ (where L is the terdentate ligand $(MeAs(C_6H_4AsMe_2)_2)$) reacted with a nitric acid solution of silver nitrate to form yellow crystals of $[Rh(NO_3)_3(L)]$ (ref. 11). It has been proposed that the *mer* stereochemistry of the precursor is retained by the nitrato product, though spectroscopic evidence for this assignment is not available.

Treatment of the dioxygen adduct $[RhCl(O_2)(L')]$ [L′ is the terdentate ligand $PhP((CH_2)_3PPh_2)_2$] with nitrogen dioxide/dinitrogen tetroxide in dichloromethane at ambient temperature afforded crystals of $[RhCl(NO_3)_2(L')]$ (ref. 56). The relatively high conductivity exhibited by this complex, together with the presence of both free and coordinated nitrate IR absorptions indicate at least the equilibrium presence of $[RhCl(NO_3)(L')]^+$.

Dilute aqueous nitric acid has been found to promote oxidation of the hydride $[RhH(PPh_3)_4]$ to yield green crystals of empirical formula $RhN_3O_7P_2C_{36}H_{30}$, initially formulated from IR and mass spectrometric fragmentation spectra as $[Rh(NO)_2(NO_3)(OPPh_3)_2]$ (ref. 57). An identical compound has been obtained by the action of concentrated nitric acid on solid $[RhH(CO)(PPh_3)_3]$, and from the reaction of $[Rh(NO)(PPh_3)_3]$ with ethanolic nitric acid in the presence of dioxygen [50], although further investigation of the products favours reformulation as $[Rh(NO)(NO_3)_2(PPh_3)_2]$ (ref. 50).

The action of warm concentrated nitric acid on a benzene solution of $[RhH(CO)(PPh_3)_3]$ afforded an intractable yellow crystalline solid which analysed for $[Rh(NO_3)_3(PPh_3)_2]$ (ref. 50).

Silver nitrate in benzene—ethanol solution at ambient temperature efficiently displaced both chloride and carbon monoxide from $[RhCl(CO)L_2(C_4(CF_3)_4)]$ giving the *trans* complex (IV) (L = $AsMe_3$ or $AsMe_2Ph$). A six coordinate state is postulated, in spite of the ambiguity of nitrate IR data, from the observation that carbon monoxide could not be easily introduced into the coordination sphere [58a].



(IV)

The reaction of the bridged complex $[RhCl_2(C_5Me_5)]_2$ with silver nitrate gave the simple substitution product $[Rh(NO_3)_2(C_5Me_5)]_n$, in which it is postulated that $n = 2$ and that the nitrates are bridging, although no spectral or molecular weight determinations have been reported [58b].

Rhodium(I). Rhodium carbonyl chloride, on shaking with anhydrous silver nitrate in petroleum ether, afforded the bridged species $[(Rh(CO)_2(NO_3))_2]$ (ref. 59) as a purple solid. Molecular weight determinations have verified the dimeric structure, and the very high IR $\nu(NO_2)$ absorptions have led to the suggestion that bridging is through nitrate.

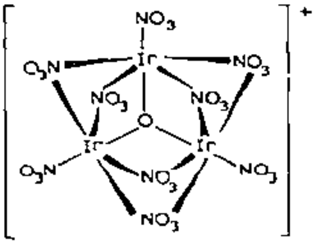
Reaction of Peone and Vaska's rhodium(I) fluoride complex [60], $[RhF(CO)(PPh_3)_2]$, with a boiling methanolic solution of an alkali metal nitrate afforded $[Rh(NO_3)(CO)(PPh_3)_2]$ as a yellow solid, probably via the solvate $[Rh(MeOH)(CO)(PPh_3)_2]^+$. The same complex has been obtained by the partial decarbonylation of the bridged species $[Rh(CO)_2(NO_3)]_2$ in the presence of excess triphenylphosphine [61]. A square planar structure, with monodentate nitrates has been assumed, and on this basis a relative assessment of metal—nitrate π-bonding has been made [61]. However, failure to consider the possibility of a five coordinate structure with bidentate nitrate renders the interpretation subject to some uncertainty (see later). At low temperatures (195 K) the complex reacted with sulphur dioxide to form the simple addition compound $[Rh(NO_3)(CO)(PPh_3)_2(SO_2)]$, though the reaction is easily reversed, sulphur dioxide being lost on warming [61].

The reaction of concentrated nitric acid with $[Rh(NO_2)(CO)(PPh_3)_2]$ afforded the bright green product "$Rh(NO)(NO_3)(PPh_3)_2$" in good yield [62]. Although it might appear that nitric acid is the nitrosyl source, as in the preparation of some ruthenium nitrosyl complexes, it has been established that many other acids will similarly attack this precursor to yield nitrosyl derivatives, and thus it is the acidic proton which reduces the nitro group [62]. However, the similarity in colour and IR absorptions between the nitrate product and the bright green complex $[Rh(NO)(NO_3)_2(PPh_3)_2]$ for which good carbon, hydrogen and nitrogen analyses have been obtained (see above) leaves the formulation "$Rh(NO)(NO_3)(PPh_3)_2$" open to some doubt.

(iv) Iridium

Iridium(IV). Alkali metal salts of the iridium(IV) anion $[Ir(NO_3)_6]^{2-}$ have been prepared by the action of dinitrogen pentoxide on the corresponding hexabromoiridate salt [63]. The potassium, rubidium and caesium salts exhibit magnetic moments consistent with the d^5 configuration, and ESR measurements on the potassium salt suggest a surprisingly high degree of metal—nitrate π-bonding [64] (see later).

Prolonged reaction of iridium tribromide with dinitrogen pentoxide has been found to yield deep purple crystals of stoichiometry $[Ir_3O(NO_3)_{10}]$. On the basis of IR and magnetic moment measurements the complex has been assigned as a trinuclear iridium(IV) cation containing bridging and unidentate nitrates, with one nitrate counter ion (V) [29].



(V)

This structure highlights the formal analogy with carboxylates and suggests that a series of trinuclear nitrato complexes analogous to the well known carboxylates should be accessible.

Iridium(III). The simple nitrate salt of iridium(III) is unknown. However, the complex anion $[Ir(NO_3)_6]^{3-}$ is formed by dissolving iridium(III) chloride in concentrated nitric acid at 373 K [8c].

The ion $[Ir(NH_3)_5(NO_3)]^{2+}$, like its rhodium analogue, has been prepared by the substitution of nitrate into the inner coordination sphere by the action of heat on the salt $[Ir(NH_3)_5(H_2O)][(NO_3)_3]$ (ref. 8c, 54).

$K_3[Ir(NO_2)_3(NO_3)_3]$ has been obtained as yellow-green crystals by treating the hexanitro iridium(III) salt with nitric acid [53]. More prolonged reaction afforded violet crystals of the hexanitrate $K_3[Ir(NO_3)_6]$. A small degree of dissociation by the nitrite anion is indicated by conductivity measurements, which show the presence of slightly more than four ions per mole of salt.

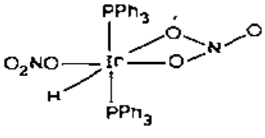
The complex $[IrCl(NO_3)_2(CO)(PPh_3)_2]$ is formed as white crystals by direct or indirect oxidative addition of $[IrCl(CO)(PPh_3)_2]$ in three separately reported reaction routes.

(a) The dioxygen adduct of Vaska's complex [66] has been found to react with nitrogen dioxide/dinitrogen tetroxide to yield the required complex [67]. A similar reaction has been observed for the triphenylarsine precursor [67].

(b) Vaska's complex itself has been shown to react directly with concentrated nitric acid in tetrahydrofuran at 313 K, forming the same dinitrato product [34], presumably accompanied by the evolution of dihydrogen. This contrasts with the reaction with perchloric acid, in which one mole of the acid was added to form $[IrClH(ClO_4)(CO)(PPh_3)_2]$ [34].

(c) Vaska's complex has been oxidised by certain metal ions in high oxidation state in the presence of nitrate ion [68]. For example, copper(II) nitrate, iron(III) nitrate and $(NH_4)_2[Ce(NO_3)_6]$ each react at ambient temperature in solution in acetone affording $[IrCl(NO_3)_2(CO)(PPh_3)_2]$. Reactions of $[IrX(CO)(PPh_3)_2]$ ($X = NCO, NCS, Br$ or N_3) proceed similarly [68].

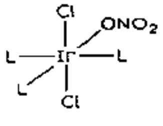
The isocyanato dinitrato product, $[Ir(NCO)(NO_3)_2(CO)(PPh_3)_2]$ was found to react slowly in an ethanol–dichloromethane solution open to the air to form $[IrH(NO_3)_2(PPh_3)_2]$ (ref. 68) as yellow crystals. An X-ray structural determination has been carried out on the latter complex which shows the phosphines to be mutually *trans*, with one monodentate and one bidentate nitrate (VI) [69]. The complex reacts with carbon monoxide affording $[IrH(NO_3)_2(CO)(PPh_3)_2]$ (ref. 69) in which both nitrato groups are now presumably monodentate. The related dinitrato cation $[Ir(NO_3)_2(CO)(PPh_2Me)_3]^+$ has been isolated as the tetrafluoroborate or perchlorate salt by the reaction of nitrogen dioxide/dinitrogen tetroxide with the dioxygen complex $[IrO_2(CO)(PPh_2Me)_3]^+$ (ref. 70) in a reaction similar to that described for the neutral species in reaction route (a).



(VI)

Electrophilic attack on the bent nitrosyl ligand by dioxygen at room temperature has produced the monosubstituted nitrates $[IrClX(NO_3)(CO)(PPh_3)_2]$ (X = I, Br, Cl, NCS, NCO or N_3) from the series of iridium(III) compounds $[Ir(NO)ClX(PPh_3)_2]$ in benzene solution [39]. This invalidates the suggestion of Marzilli and Trogler [71], that nitrite rather than nitrate would form on oxidation of nitrosyls exhibiting low frequency ν(NO) IR absorptions, since here ν(NO) frequencies of the precursors are low (1520—1560 cm^{-1}) and nitrato products are nevertheless obtained. The stoichiometry of the precursor is obviously a more important consideration.

Mer$[IrCl_3L_3]$ (L = PMe_2Ph, PEt_2Ph or $AsMe_2Ph$) reacted with silver nitrate in acetone—water solution, substituting the chloride labilised by virtue of its position *trans* to phosphine or arsine [72], to form the complex (VII) in which nitrate has been shown to exhibit exceptionally good leaving group properties (see later). A similar product has been obtained from the triiodide for L = PMe_2Ph.



(VII)

The reaction of $[Ir(NO)(PPh_3)_3]$ or $[Ir(NO)(CO)(PPh_3)_2]$ with ethanolic nitric acid afforded green crystals of $[Ir(NO)(NO_3)_2(PPh_3)_2]$ (ref. 50). The low IR frequency attributable to ν(NO) suggests the product to be an iridium(III) complex containing the bent M—N—O moiety.

An intractable yellow crystalline solid, having elemental analysis consistent with the formulation $[Ir(NO_3)_3(PPh_3)_2]$, has been obtained by treating a benzene solution of $[IrH(CO)(PPh_3)_3]$ with warm concentrated nitric acid [50].

Iridium(I). $[IrCl(CO)(PPh_3)_2]$ reacted with sodium nitrate to give a variety of products of indeterminate character [60]. With silver nitrate in acetone, however, $[Ir(NO_3)(CO)(PPh_3)_2]$ was obtained [13]. This was surprising in view of the fact that other simple metal nitrates had induced oxidative addition to yield the iridium(III) bis(nitrato) complex (see above), the metal counter ion itself being reduced. Thus the reaction

$$[IrCl(CO)(PPh_3)_2] + 2\ AgNO_3 \rightarrow [IrCl(NO_3)_2(PPh_3)_2] + 2\ Ag$$

does not occur under these conditions. However, previous workers on this system found silver metal to be deposited [74], though the conditions were not reported. $[Ir(NO_3)(CO)(PPh_3)_2]$ has also been prepared by metathesis of Peone and Vaska's fluoro complex, $[IrF(CO)(PPh_3)_2]$, employing alkali metal nitrates in boiling methanol [60]. Like the chloride, the resulting nitrate has also been found to add sulphur dioxide and dioxygen under mild conditions, affording $[Ir(NO_3)(SO_2)(CO)(PPh_3)_2]$ and $[Ir(NO_3)(O_2)(CO)(PPh_3)_2]$ respectively [13]. The latter complex itself undergoes addition with sulphur dioxide yielding $[Ir(NO_3)(SO_4)(CO)(PPh_3)_2]$ (ref. 13). The sulphur dioxide derivative is formed reversibly, but the dioxygen complex, which is formed by an irreversible addition, rapidly decomposes in solution to intractable products, although as a solid it remains intact for several days.

The related complex $[Ir(NO_3)(CO)(PBu^t{}_2Pr^n)_2]$ has been obtained by the action of methanolic nitric acid on the complex $[Ir(OH)(CO)(PBu^t{}_2Pr^n)_2]$ (ref. 75).

(v) Palladium

Commercial $[Pd(NO_3)_2]$ reacts with dinitrogen pentoxide to afford anhydrous $[Pd(NO_3)_4]$, the first simple salt of palladium(IV). This product is hydrolysed by water vapour to afford $[Pd(OH)_2(NO_3)_2]$, and is reduced by dinitrogen tetroxide to form the adduct $[Pd(NO_3)_2 \cdot 2\ N_2O_4]$ (ref. 73).

The hydrated palladium(II) nitrate, $Pd(NO_3)_2 \cdot 2\ H_2O$, has been obtained as a brown powder by the direct reaction of the metal with concentrated nitric acid [52].

There are two reported examples of simple palladium(II) nitrato species. The action of anhydrous dinitrogen pentoxide on hydrated palladium(II) nitrate afforded the anhydrous nitrate, $Pd(NO_3)_2$, as a volatile brown solid [76]. The tetranitrato palladate ion, $[Pd(NO_3)_4]^{2-}$, has been isolated as its potassium salt in the form of orange-red crystals from the stoichiometric reaction of palladium metal with potassium nitrate in concentrated nitric acid, and from the reaction of concentrated nitric acid with the potassium salt of the anhydrous tetranitro palladate ion, $[Pd(NO_2)_4]^{2-}$ (ref. 77).

Reaction of $K_2[Pd(NO_2)_4]$ with ammonium nitrate in the presence of ammonium sulphate has been reported to form *trans*$[Pd(NO_3)_2(NH_3)_2]$ (ref. 78). A number of related dinitrato complexes have been prepared in which *cis* stereochemistry is necessitated by the coordination of a bidentate amine ligand. For example, yellow crystals of $[Pd(NO_3)_2(2,2'\text{bipyridyl})]$ have been obtained by the action of bipyridyl on palladium(II) nitrate in aqueous solution [79—81]. The considerable splitting of the nitrate IR absorptions for this complex is thought to be a feature of *cis* nitrato groups [52]. A related mononitrato derivative, $[Pd(NO_3)(CH_3CO_2)(2,2'\text{bipyridyl})]$, prepared as orange crystals by the action of nitrogen dioxide/dinitrogen tetroxide on $[Pd(CH_3CO_2)_2(2,2'\text{bipyridyl})]$ in acetic acid, has been shown to catalyse the acetoxylation of chlorobenzene [80] (see later).

Similar yellow crystalline compounds, $[Pd(NO_3)_2(\text{phen})]$ (phen = 1,10 phenanthroline or 2,9 dimethylphenanthroline), have been synthesised by direct reaction of palladium(II) nitrate with the ligand in nitric acid [12], and conductivity measurements on the products indicate no ionic dissociation. The absence of ionic nitrate is confirmed by IR spectroscopy. However, IR and conductivity measurements on the compound "$Pd(NO_3)_2(\text{phen})(H_2O)$", prepared by hydrolysis of the former complex, indicate the ionic formulation $[Pd(NO_3)(\text{phen})(H_2O)]^+(NO_3)^-$ for this complex [12]. Reaction of the non-ionic phenanthroline complexes with an excess of the two ligands has been found to yield pink deposits with stoichiometry $[Pd(NO_3)_2(\text{phen})_2(H_2O)_x]$

(x = 2 in the case of the phenanthroline complex, and 1 in the case of the dimethylphenanthroline derivative). Again for these complexes IR and conductimetric data suggest one ionic and one coordinated nitrate group.

Similarly, the direct reaction of palladium(II) nitrate with pyrazine (pz) or 2-chloro-3-methylpyrazine (cmp), in the molar ratio of ligand to salt of 2 : 1, formed $[Pd(NO_3)_2(pz)]_n$ and $[Pd(NO_3)_2(cmp)]_n$ (ref. 82). Reaction of the nitrate with the related ligands 2,6-dimethylpyrazine (dmp) and 2-methylpyrazine (mp), in the same molar ratio, however, afforded the bis-substituted complexes $[Pd(NO_3)_2(dmp)_2]$ and $[Pd(NO_3)_2(mp)_2]$ (ref. 82). In the absence of spectral or conductimetric data it is difficult to find a satisfactory explanation for the differing degrees of substitution. Controlled decompositions of these pyrazine complexes were found to be highly exothermic as a result of the oxidising nature of the nitrate ligands.

The stoichiometric reaction of palladium(II) nitrate with isoxazole ($\overline{\mathrm{O{-}N{=}CH{-}CH{=}C}}\mathrm{H}$) or with 3,5-dimethylisoxazole in refluxing acetone gave $[Pd(NO_3)_2(isox)_2]$ as pale yellow non-conducting products [83]. In both complexes the isoxazole ligands are monodentate, and a *trans* square planar geometry is probable, both by analogy with the halo complexes (metal—halide vibrational frequencies indicate *trans*) and from the absence of splitting in the nitrate IR absorptions [52].

Two nitrosyl nitrato complexes have been reported, both of which appear to contain linear M—N—O moieties [84]. The anion $[Pd(NO)(NO_2)_4(NO_3)]^{2-}$ has been isolated as the red crystalline potassium salt from the reaction of $K_2[Pd(NO_2)_4]$ with hot concentrated nitric acid [84]. The reaction of nitrogen monoxide and methanol vapour with solid palladium(II) nitrate has been reported to form a solid black diamagnetic impure sample of "$Pd(NO)_2(NO_3)_2$" [84].

Tertiary phosphines react with palladium(II) nitrate to form square planar derivatives. Reported examples include $[Pd(NO_3)_2(PEt_3)_2]$ and $[Pd(NO_3)_2(PEt_2Ph)_2]$ (ref. 85). Excess phosphine leads to the formation of $[Pd(PPh_3)_4]$ (ref. 86). $[Pd(NO_3)_2(PPh_3)_2]$ has been prepared by the reaction of $[PdO_2(PPh_3)_2]$ with nitrogen dioxide/dinitrogen tetroxide [36], and by the prolonged reaction of isoamylnitrite with $[Pd(N_3)_2(PPh_3)_2]$ (ref. 87). In none of these cases has the stereochemistry been elucidated. However, $[Pd(NO_3)_2(PBu^t{}_2H)_2]$, prepared as a yellow solid by the reaction of di(tert.-butyl)phosphine with palladium(II) nitrate [40] is believed to be *trans* by analogy with a number of similarly prepared dihalo derivatives, for which the high $^2J(PP)$ coupling constants (calculated from the proton NMR spectra) indicate *trans* configuration. Similarly, $[Pd(NO_3)(CH_3CO)(PEt_3)_2]$ has been assigned a *trans* configuration [121] by comparison with the halo derivatives, whose *trans* structure was inferred from dipole moment measurements [88].

Trans$[PdH(NO_3)(Pcy_3)_2]$ (cy = cyclohexyl) has been prepared via the yellow form of $[Pd(NO_3)_2(Pcy_3)_2]$ by mixing palladium(II) nitrate with ethanolic tricyclohexylphosphine below 243 K, followed by slow reaction with sodium borohydride at 293 K [69]. Above 243 K the green form of the dinitrate was obtained, which showed no reaction with sodium borohydride. The nitrate group of the hydride complex is particularly labile by virtue of its position *trans* to hydride, and has proved a useful reagent in the preparation of cationic square planar palladium complexes [89] (see later).

Treatment of $[Pd(Me_2S)_2Cl_2]$ in refluxing dimethyl sulphide—aqueous ethanol in the presence of silver nitrate and the quadridentate ligand tris(*o*-diphenylarsinophenyl)arsine (qas) afforded $[Pd(NO_3)(qas)]^+$, which was isolated as the deep red crystalline perchlorate with trigonal bipyramidal structure [90].

Ethanolic palladium(II) nitrate with *o*-phenylenebis(diphenylstibine) gave the product $[Pd(NO_3)_2(Sb—Sb)_2]$ (where Sb—Sb is the bidentate distibine ligand) as fawn crystals [91]. The same complex has been obtained by metathesis from the chloride. The solid state IR data suggest a square planar cation, $[Pd(Sb—Sb)_2]^{2+}$, since both nitrates are shown to be ionic. However, in solution conductivity measurements indicate appreciable amounts of pentacoordinate $[Pd(NO_3)(Sb—Sb)_2]^+$, the presence of coordinated nitrate being confirmed by IR. Pentacoordination is favoured in this complex, relative to arsine or phosphine analogues, by the lower electronegativity of the stibine ligand. This permits a lower effective positive charge on the metal, which in turn facilitates the *dsp*^{3} hybridisation of a pentacoordinate state [92].

The orange-yellow crystalline product, $[Pd(NO_3)_2(Me_2SO)_2]$, obtained by the reaction of palladium(II) nitrate with dimethyl sulphoxide [93] has been shown by X-ray crystallographic determination to possess *cis* geometry. This is in contrast to the *trans* configuration of the dichloro derivative [94], and thus casts doubt on the inferred *trans* arrangement of some other palladium nitrato complexes that have been assigned by similar analogy (see above).

Complexes *trans*$[Pd(NO_3)_2(R_2S)_2]$ (R = P[illegible] or Pr) have been obtained by shaking aqueous solutions of the sulphide with palladium(II) nitrate [95,99]. A relative estimate of the degree of metal—nitrate π-bonding has been made from the ^1H NMR of these complexes (see later).

(vi) Platinum

No simple platinum nitrates appear to have been isolated [24,65]. However, the vast array of known platinum(II) and platinum(IV) complexes include many species containing nitrate anions in the inner coordination sphere. Early work in this field has been comprehensively surveyed [65].

Platinum(IV). With the possible exception of trimethyl platinum nitrate [160], all nitrato complexes of platinum(IV) are of the "classical" type in which the nitrate group is coordinated along with aquo, ammino, nitro or halo ligands. The reaction of dinitrogen pentoxide with potassium hexabromoplatinate has afforded the diamagnetic platinum(IV) hexanitrato complex $K_2[Pt(NO_3)_6]$ (ref. 63), the only species containing platinum coordinated exclusively by nitrate ligands.

The platinum(II) nitro complex $K_2[Pt(NO_2)_4]$ is oxidised by nitric acid to yield $K_2[Pt(NO_2)_6]$ (ref. 183, 184). Both of these complexes have been widely

TABLE 1

A selection of platinum (IV) ammino and related complexes containing nitrate ligands

Complex	Ref.[a]
trans$[Pt(NO_3)_4(NH_3)_2]$	
$[Pt(NO_3)_3(OH)(NH_3)_2]$	144
$[Pt(NO_3)_2(NH_3)_4]^{2+}$	
$[Pt(NO_3)_2(OH)(NH_3)_3]^+$	
$[Pt(NO_3)_2Cl(NH_3)_3]^+$	
trans$[Pt(NO_3)_2(OH)_2(NH_3)_2]$	
trans$[Pt(NO_3)_2(NO_2)_2(NH_3)_2]$	
$[Pt(NO_3)_2Cl_2(NH_3)_2]$	97
$[Pt(NO_3)_2Br_2(NH_3)_2]$	97
$[Pt(NO_3)_2ClBr(NH_3)_2]$	144
$[Pt(NO_3)_2(OH)_2(en)]$	157
$[Pt(NO_3)_2(NO_2)_2(en)]$	158
$[Pt(NO_3)(OH)(NH_3)_4]^{2+}$	
$[Pt(NO_3)Cl(NH_3)_4]^{2+}$	
$[Pt(NO_3)(CO_3)(NH_3)_4]^+$	
$[Pt(NO_3)(OH)_2(NH_3)_3]^+$	
$[Pt(NO_3)Cl(NO_2)_2(NH_3)_2]$	
$[Pt(NO_3)Cl_2(OH)(NH_3)_2]$	98
$[Pt(NO_3)Cl_2(NO_2)(py)_2]$	99
$[Pt(NO_3)(NO_2)_3(en)]$	158
$[Pt(NO_3)_2Cl_2(en)]$	190
$[Pt(NO_3)Cl_3(en)]$	190
$[Pt(NO_3)BrCl(en)]$	190
$[Pt(NO_3)Cl_2(NO_2)(en)]$	191
$[Pt(NO_3)_2(CN)_2(en)]$	193
$[Pt(NO_3)(NO)(NO_2)_4]^{2-}$	114
$[Pt(NO_3)(NO)(NO_2)_2(NH_3)_2]$	114
$[Pt(NO_3)(NO)(NO_2)_2(en)]$	114
$[Pt(NO_3)(NO)(en)_2]^{2+}$	114

[a] Ref. 1 unless otherwise stated.

employed to synthesise mixed nitro/nitrato derivatives. Several papers [77,96, 183,184] report the conversion of $K_2[Pt(NO_2)_4]$ to $K_2[Pt(NO_2)_3(NO_3)_3]$. However, there is some controversy concerning the reaction conditions necessary to obtain a single pure product [183]. Authentic $K_2[Pt(NO_2)_3(NO_3)_3]$ appears to possess a facial configuration [185], and undergoes solvolysis in aqueous nitric acid to afford $K_2[Pt(OH)_3(NO_3)_3]$ (ref. 186). The mixture of products originally formulated as $K_2[Pt(NO_2)_3(NO_3)_3]$ has been reported to afford $K_2[Pt(OH)_2(NO_3)_4]$ on solvolysis [77]. The same dihydroxy complex was obtained from the stoichiometric reaction of potassium nitrate with $PtO_2 \cdot H_2O$ in concentrated nitric acid [77]. The yellow product, obtained from the reaction of $K_2[Pt(NO_2)_4]$ with concentrated nitric acid, and originally formulated [84] as a platinum(II) nitrosyl nitrato complex $K_2[Pt(NO)(NO_3)(NO_2)_4]$, has been identified as the platinum(IV) hexanitro salt $K_2[Pt(NO_2)_6]$ (ref. 101). It seems probable that $K_2[Pt(NO)(NO_3)(NO_2)_4]$ is responsible for the transient blue colour observed in this synthesis, and is rapidly isomerised to yellow $K_2[Pt(NO_2)_6]$ on further heating [101]. A similar isomerisation process is thought to occur in the conversion of $[Pt(NO)(NO_3)(NH_3)_4]^{2+}$ to $[Pt(NO_2)_2(NH_3)_4]^{2+}$ (ref. 101). In connection with their studies of *trans* effects in platinum(IV) chemistry, Chernyaev et al. have synthesised a variety of platinum(IV) nitrato complexes including the species $[Pt(X, NO_3)(Y, NO_3)(NH_3)_2]$ (X, Y = anionic ligands, *trans* ligand pairs in parenthesis) (ref. 144, 180—182), $[PtY_2(NO_3)_2en]$, $[PtY_2(NO_2)(NO_3)en]$ and $[PtY_3(NO_3)en]$ (Y = halide) (ref. 187, 190, 191). In all cases, the nitrate ligands are labile and subject to facile hydrolysis (97—99), but certain trends are observed. In particular, the nitrate ligands are more readily hydrolysed when the pair of ammine ligands are mutually *cis*, and the ease of hydrolysis of the nitrate group on a *trans* X—Pt—NO_3 axis increases as the *trans*-effect of X decreases. In accordance with this observation, *trans*-dinitrate groupings are particularly labile in both *cis* and *trans* diammine complexes.

Platinum(II). The cherry red product "$K_3[Pt_2(NO_2)_6(NO_3)_3]$", derived from $K_2[Pt(NO_2)_6]$ and nitric acid under carefully controlled conditions, has been formulated as the binuclear nitrate-bridged platinum(II)/(IV) complex $K_3[(O_2N)_3Pt(NO_3)_3Pt(NO_2)_3]$ (ref. 188). A similar nitrato-bridged platinum(II) complex $K_2[(O_2N)_2Pt(NO_3)_2Pt(ONO)_2]$, also cherry red in colour, has been obtained by evaporation of an aqueous solution of $K_2[Pt(NO_2)_4]$ containing two moles of nitric acid [189]. The blue nitrosyl nitrato complex $[Pt(NO)(NO_3)(NH_3)_4][NO_3]_2$, first prepared by oxidising $[Pt(NH_3)_4][NO_3]_2$ with concentrated nitric acid [192], has more recently been obtained by the action of liquid dinitrogen tetroxide on $[Pt(NH_3)_4][NO_3]_2 \cdot H_2O$ (ref. 100) or by treatment of $[Pt(NH_3)_4]Cl_2$ with nitrogen monoxide in nitric acid [84]. In common with some other nitrosyl nitrato complexes of platinum(II) (see above) it undergoes isomerisation to a platinum(IV) dinitro derivative [101].

Amine complexes $[Pt(NO)(NO_3)A_4]^{2+}$ (A = $MeNH_2$, $PhNH_2$ or 0.5 (1,2-diaminoethane)) analogous to the tetrammine have been similarly prepared [102—104]. Finally the treatment of $K_2[Pt(NO_2)_4]$, $[Pt(NO_2)_2(NH_3)_2]$, $[Pt(NO_2)_2(en)]$ and $[Pt(en)_2][NO_3]_2$ with concentrated nitric acid under nitrogen at ambient temperature affords the air sensitive blue-green nitrosyl—nitrato complexes $K_2[Pt(NO_3)(NO)(NO_2)_4]$, $[Pt(NO_3)(NO)(NO_2)_2(NH_3)_2]$, $[Pt(NO_3)(NO)(NO_2)_2(en)]$ and $[Pt(NO_3)(NO)(en)_2][NO_3]_2$ respectively [114]. These products are rapidly decolourised by water, dilute acid, alcohol and ether. Treatment with concentrated hydrochloric acid leads to replacement of labile nitrate (*trans* to nitrosyl) by chloride [114].

$[Pt(OH)_2(2,2'bipyridyl)]$, on treatment with nitric acid, has been shown to undergo a stepwise substitution of the hydroxy groups by nitrate [105], the disubstituted product forming only at acidities greater than pH 4. The related *cis* diammine, $[Pt(NO_3)_2(NH_3)_2]$ has been obtained by metathesis from the cancer inhibiting complex *cis*$[PtCl_2(NH_3)_2]$. However, the chemotherapeutic activity of the nitrato complex is greatly reduced [106], and the complex additionally displays neuro-toxicity [55]. The complex $[Pt(OH)(NO_3)(NH_3)_2]$ has been reformulated as $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2][NO_3]_2$ ref. 106.

Both *cis* and *trans* forms of the bis phosphine complexes $[Pt(NO_3)_2(L)_2]$

(L = phosphine or thioether) have been prepared by metathesis with silver nitrate from the chloro or iodo derivatives [99]. The expected difference between dipole moments of the *cis* and *trans* forms of these products has been observed [1,142]. However, the *trans* isomer has been found to possess a small but significant dipole, suggesting that the *trans* nitrato groups may not be symmetrically coordinated.

The *cis* isomer of the triphenylphosphine derivative has been obtained indirectly from $[Pt(PPh_3)_4]$ via the dioxygen complex $[Pt(PPh_3)_2O_2]$ by treatment with nitrogen dioxide/dinitrogen tetroxide at ambient temperature. The product was found to be readily hydrolysed by boiling water [36].

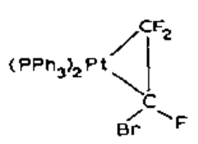
The addition of solid $NOBF_4$ to a suspension of the dioxygen complex $[Pt(PPh_3)_2O_2]$ in acetonitrile readily formed a clear red solution of $[Pt(NO_3)(PPh_3)_2]^+$ (ref. 107) in a reaction analogous to the carbonylation of the same precursor to $[Pt(CO_3)(PPh_3)_2]$ (ref. 108).

Singly substituted complexes have been isolated in which nitrate coexists with another anionic ligand. In no case, however, has the reaction been accomplished by substitution of the anion into a bis nitrato complex. The products *trans*$[PtH(NO_3)(L)_2]$ (L = triethylphosphine or triethylarsine) were obtained by the metathetical reaction of *trans*$[PtHCl(L)_2]$ with silver nitrate in aqueous methanol [109,110]. The methyldiphenylphosphine derivative has been similarly obtained from *trans*$[PtHI(PMePh_2)_2]$ (ref. 111).

The labile *trans* nitrate group of these hydrido complexes is believed to enhance the insertion of alkenes into the metal—hydride bond. Thus, for example, addition of ethene to an acetone solution of $[PtH(NO_3)(PMePh_2)_2]$ at ambient temperature and pressure readily forms the *trans* alkyl $[Pt(C_2H_5)(NO_3)(PMePh_2)_2]$ (ref. 112). The related methyl complex $[Pt(CH_3)(NO_3)\cdot(L)_2]$ (L = triethylphosphine) had previously been prepared by metathesis with silver nitrate on $[PtI(CH_3)(L)_2]$, (ref. 113). The triphenylphosphine analogue $[Pt(CH_3)(NO_3)(PPh_3)_2]$ has been obtained, again via the *trans* methyl iodo complex, by treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with methyl iodide, followed by metathesis with silver nitrate as before. *Trans*$[Pt(CF_3)(NO_3)(PMe_2Ph)_2]$ has been similarly obtained from the corresponding fluorinated alkyl iodide [115].

Related aryls, *trans*$[Pt(Ar)(NO_3)(PEt_3)_2]$ (Ar = phenyl, *ortho*-tolyl or mesityl), have similarly been isolated by metathesis [116]. ^{19}F NMR data from the pentafluorophenyl derivative [1] indicates a surprisingly high degree of π-bonding in the metal—nitrate interaction (see later).

Trans$[Pt(NO_3)(CF{:}CF_2)(PPh_3)_2]$ has been obtained as white crystals from the prolonged reaction of potassium nitrate with complex(VIII) in boiling acetone [117], probably by initial nucleophilic attack by nitrate onto the

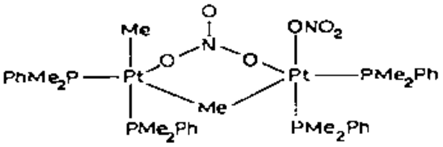


(VIII)

metal centre, followed by vinyl rearrangement.

Two alkyl nitrato complexes have been synthesised for which chelation by bidentate phosphine has dictated *cis* geometry. Treatment of [Pt(CH_3)$_2$(1,5-cyclooctadiene)] with hydrochloric acid and (1,2-diphenylphosphino)ethane (dpe) followed by aqueous silver nitrate afforded pale crystals of *cis*[Pt(NO_3)(CH_3)(dpe)]. Similarly, *cis*[Pt(NO_3)(CH_3)(pdmp)] (pdmp = 1,2-phenylenebis(dimethylphosphine)) has been obtained by metathesis of the chloride with silver nitrate [118].

A novel preparation of this type of complex has been achieved by alkyl/nitrate exchange. On mixing dichloromethane solutions of *cis*[Pt(CH_3)$_2$(PMe_2Ph)$_2$] and *cis*[Pt(NO_3)$_2$(PMe_2Ph)$_2$] rapid exchange occurred to form *cis*[Pt(CH_3)(NO_3)(PMe_2Ph)$_2$] (ref. 119) as the initial product. However, this product slowly isomerised to the (presumably) more stable *trans* form. The observed kinetic preference for the *cis* isomer suggests the existence of a cyclic intermediate with both bridging nitrate and alkyl(IX).



(IX)

Unsaturated hydrocarbons are also known to insert into the metal alkyl bond [120]. Thus, for example, [Pt(RC:CRMe)(NO_3)(LL)] (LL = 1,2-phenylenebis(dimethylphosphine)) is readily formed at ambient temperature by the addition of the appropriate acetylene to [Pt(CH_3)(NO_3)(LL)] (ref. 118).

The insertion of carbon monoxide into the metal—alkyl bond, followed by metathesis with silver nitrate, has yielded [Pt(MeCO)(NO_3)(PEt_3)$_2$] from [Pt(CH_3)Cl(PEt_3)$_2$] (ref. 121).

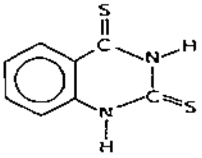
Treatment of the tetrafluoroborate salt of the cationic dimer {PtCl(L)$_2$}$_2^{2+}$ (L = PEt_3, PPh_3, PMe_2Ph) with sodium nitrate has been found to yield white crystals of *cis*[PtCl(NO_3)(L)$_2$] (ref. 122). The triphenylphosphine product may then be converted into a bridged nitrato analogue of its chloro precursor [Pt_2(NO_3)$_2$(PPh_3)$_4$](BF_4)$_2$ by reaction with boron trifluoride in a sealed tube. The action of carbon monoxide on this dimer, or the action of silver tetrafluoroboron and carbon monoxide on the products *cis*[PtCl(NO_3)(L′)$_2$] (L′ = PEt_3 or PMe_2Ph) afforded [Pt(NO_3)(CO)(L′)$_2$](BF_4) as white crystalline solids. A *trans* structure has been postulated by analogy with the known chloro derivatives. The carbonyl group of the triphenylphosphine product was found to undergo nucleophilic addition by methanol [121], forming a methoxycarbonyl complex, [Pt(COOMe)(NO_3)(PPh_3)$_2$].

The phosphonate, [Pt(NO_3)(($PhO)_2PO$)(Bu_3P)$_2$], has been obtained by metathesis from the chloro complex with silver or sodium nitrate [33], and the relatively low $^2J(PP')$ coupling suggests phosphonate *cis* to phosphine, thus indicating a *trans* geometry for the complex. *Trans*[Pt(NO_3)-*trans*-

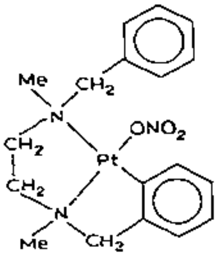
$(HC{:}CHR)(PPh_3)_2]$ (R = H or Ph) was indirectly obtained as colourless crystals from $[Pt(PPh_3)_3]$ via the bromo intermediate by treatment with bromoethene (for R = H) or 1-bromo-2-phenylethene (for R = Ph) followed by metathesis with silver nitrate in aqueous acetone [123]. A similar *trans* complex was obtained by the insertion of phenylpropyne into the metal—hydride bond of *trans*$[PtH(NO_3)(PEt_3)_2]$ (ref. 124) in which again the alkenyl group shows a *trans* disposition of Pt and Ph (see later).

Solid state IR shows the platinum(II) salt $[Pt(SbPh_3)_4](NO_3)_2$ to contain only ionic nitrate. However, conductimetric measurements indicate extensive association to form the five coordinate cation $[Pt(SbPh_3)_4(NO_3)]^+$ in solution [92]. As in the case of similar palladium stibine complexes, this state is stabilised by the lower electronegativity (relative to arsine or phosphine) of the stibine ligands (see above). The cation $[Pt(NO_3)(qas)]^+$ [qas = $As(o\text{-}C_6H_4AsMe_2)_3$] has been assigned a trigonal bipyramidal structure [90].

Nitric acid is reported to react with the thioquinazoline complex $[Pt(Q)_2(PPh_3)_2]$ (Q = quinazoline(^{1}H,^{3}H)-2,4-dithione,(X)) affording the diamagnetic product $[PtH(NO_3)(Q)_2]$ (ref. 125) as a yellow solid. However, no satisfactory explanation has been offered for the exceptionally high $\nu(NO_2)$ IR absorption (1690 cm^{-1}) of this apparently monodentate nitrato complex.


(X)

Metathesis of the internally metallated complexes *trans*[PtCl(P—C)(L)] (P—C = $C_6H_4PBu^t_2$, L = PBu^t_2Ph or P—C = $CH_2C_6H_4PBu^t(o\text{-tolyl})$, L = $PBu^t(o\text{-tolyl})_2$) with silver nitrate afforded colourless prisms of $[Pt(NO_3)(P\text{—}C)(L)]$. The good leaving group property of nitrate was confirmed by the relative ease with which the *ortho*-tolyl derivative of the nitrato complex underwent further metallation to $[Pt(P\text{—}C)_2]$ (ref. 126). The bridged metallated species $[Pt_2Cl_2(CH(Me)C_6H_4PBu^t_2)_2]$, on treatment with silver nitrate, yielded a product of stoichiometry $[Pt(NO_3)(CH(Me)C_6H_4PBu^t_2)]$ (ref. 127). Although the molecular weight determination in chloroform solution is consistent with


(XI)

monomeric formulation, it is possible that the solid complex is nitrate bridged. However, IR data is not capable of conclusively differentiating between bridged and bidentate nitrate coordination.

The complex $[Pt(NO_3)(PhCH_2(Me)N(CH_2)_2N(Me)CH_2Ph)]$ (XI), prepared by metathesis from the chloro derivative, was found not to undergo further *ortho*-metallation in spite of the better leaving group property of nitrate [128].

D. DEGREE OF π-BONDING

It has been widely accepted that the degree of π-bonding in the metal—nitrate bond is negligible [1]. However, determinations of π-interactions in platinum metal—nitrate bonds have produced conflicting conclusions.

Peone and Vaska [60] have devised a relationship between the 'total electronegativity' (both conventional σ-electronegativity and the electronegativity caused by the π-acidity of the ligand) of an anionic ligand, X, and the IR carbonyl frequency in the square planar complexes *trans*$[MX(CO)(PPh_3)_2]$ (M = Rh or Ir). By calculating both this total electronegativity from the observed $\nu(CO)$ frequency and the σ-electronegativity from $\nu(X—H)$ of the compound HX using Wilmshurst's relationship [129], a value may be obtained for the electronegativity of π-acidity. An order of decreasing π-acidity thus obtained, $I > Br > CN > Cl > NO_2 > NCS \approx N_3 > ONO_2 > OCOR > OH \approx F$, supports the view that nitrate is virtually unable to engage in metal—ligand π-bonding.

Similarly, Fergusson and co-workers [95,130] suggested that the ^1H NMR chemical shifts of the alpha hydrogen nuclei in the square planar complexes trans$[PdX_2(R_2Y)_2]$ (where X = anionic ligand, Y = S, Se or Te, R = ethyl, propyl or n-butyl) are qualitatively related to the degree of π-acidity exhibited by X. High π-acidity tends to increase the electronegativity of the metal and thus draws electron density from the alpha protons of the R_2Y ligands. Comparisons between the data for X = NO_2, Cl, Br, I and NO_3 shows a trend for decreased alpha proton shielding $NO_3 > NO_2 > I$ for $R_2Y = Pr_2S$, and $NO_2 > Cl > Br > I$ for $R_2Y = Et_2S$, again indicating a low π-acidity for bound nitrate.

However, ESR measurements [63] on the octahedral complex $K_2[Ir(NO_3)_6]$ give a surprisingly high value of $f_\pi = 0.38$ for the metal—ligand π-interaction. A similarly high value was obtained by ^{19}F NMR studies [1] of *trans*$[PtX(C_6F_5)(Et_3P)_2]$ (X = anionic ligand) which suggested nitrate exhibited π-acidity comparable to cyanide.

An infrared [$\nu(C—O)$] investigation by Varshavskii and co-workers [61] of rhodium(I) and rhodium(III) compounds suggested that for nitrate the degree of π-interaction may be especially dependent on the stereochemistry of the complex concerned. In the square planar complexes *trans*$[RhX(CO)(PPh_3)_2]$ (X = anionic ligand) the existence of three bonding conditions of the carbonyl to the metal is suggested: (i) a dative σ-bond between lone pair electrons on carbon and dsp^2 hybrid metal orbital; (ii) dative π-bonding of the filled d_{xy} and d_{xz} metal orbitals with the two vacant antibonding orbitals of the carbonyl molecule; and (iii) dative bonding of the filled bonding π-orbitals of the carbonyl molecule with the vacant metal p_z orbital.

It has been established that this latter interaction is important in the Ni—C bond of $[Ni(CN)_4]^{2-}$ (ref. 131). Following the suggestion that it is primarily the π-interactions that affect the value of ν(C—O) [132], the order of increasing ν(C—O) obtained for X = F < Cl < Br < NO_3 < I < SCN has been interpreted as a series of increasing π-acceptor power of the anionic ligands. However, the order of ν(C—O) values for the rhodium(III) oxidative addition complexes $[RhX(CO)(SO_2)(PPh_3)_2]$ is identical to the former with the exception of nitrate: F < NO_3 < Cl < Br < SCN (ref. 61).

In the square planar rhodium(I) complex, the nitrate π-bonding orbitals show correct symmetry to interact with the vacant p_z metal orbital, provided that complex and ligand are coplanar. Thus some nitrate π-electron density could be transferred to the p_z orbital, reducing its acceptor strength for carbonyl π-bonding orbitals (bonding condition (iii) above). The resultant strengthening of the C—O bond and increase in ν(C—O) frequency, rather than being illustrative of π-acidity of the nitrato group, might in fact be due to the very opposite effect of π-donation to the metal. In the rhodium(III) complex the p_z orbital is no longer vacant, this latter interaction is therefore at least considerably reduced, and the "π-acidity" of the nitrate is now seen to be negligible and comparable to fluoride. A similar explanation might account for the apparent high metal—nitrate π-bond in square planar *trans*$[Pt(NO_3)(C_6F_5)(Et_3P)_2]$ (see above), in which the bonding π-orbitals of coplanar nitrate and pentafluorobenzene ligands possess correct symmetry for a similar interaction with the metal p_z orbital.

The results for the rhodium complexes must, however, be treated with caution, since the possibility that $[Rh(NO_3)(CO)(PPh_3)_2]$ might contain bidentate nitrate has not been ruled out, so that the exceptional position of the ligand in the square planar series could be a result of its different, pentacoordinate geometry.

Finally, calculation of C—O stretching force-constants and interaction constants using the Cotton—Kraihanzel method, and Graham's σ- and π-parameters, shows the nitrate group to act as a σ-acceptor and π-donor in $[Re(CO)_5(NO_3)]$, relative to the methyl group used as a standard. The σ-donor power is less than that of the halogens but the π-acceptor power is intermediate between that of chloride and bromide [147].

E. *TRANS* INFLUENCE, *TRANS* EFFECT AND *CIS* INFLUENCE

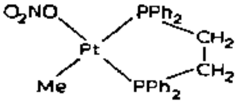
The high value of ν(Pt—C) for the nitrato derivative in the series of complexes *trans*$[PtMeX(PR_3)_2]$ (X = anionic ligand, R = CH_3 or C_2H_5) is consistent with a low position in the *trans* influence series for the ligand [133].

Analysis of ν(Pt—H) [111,134] in the complexes *trans*$[PtHX(L)_2]$ (X = anionic ligand, L = PEt_3 or PPh_2Me) have been used to determine series of *trans* influence. Again, a high *trans* influence of X should reduce the bond strength and thus the IR frequency of the Pt—H vibration *. Series of decreasing ν(Pt—H) values confirm the low *trans* influence of nitrate: $NO_3 \approx OCOCF_3 > NCS > Cl > Br > I > NO_2 > SCN > CN$.

A plot of ν(Pt—H) against τ(Pt—H) (^{1}H NMR) [111] shows an approximately linear relationship between the two quantities for the complexes *trans*-[PtHX(L)$_2$] (L = PPh_3 or PPh_2Me), indicating a direct relationship between the strength of the Pt—H bond * and the shielding of this proton. The low *trans* influence of nitrate thus leaves electron density in the vicinity of the hydridic proton, and is exhibited by the order of increasing chemical shift (increasing *trans* influence) for the complexes [PtHX(PEt$_3$)$_2$] (refs. 109,110) where nitrate is again found to cause the highest shielding. In contrast, it has been reported [135] that ^{195}Pt chemical shifts for these complexes bear an inverse relationship to the proton shifts, the metal nucleus of the nitrato complex experiencing the poorest shielding effect.

Although in these platinum metal hydrido complexes no relationship was found between ^1J(Pt—H) or ^2J(P—H) and *trans* influence, a good correlation has been obtained for ^1J(Pt—P) in the complexes *trans*[PtX((PhO)$_2$PO)·(Bu$_3$P)$_2$] (ref. 137). The ^1J(Pt—P) coupling constant has been interpreted as a measure primarily of the contribution of the platinum 6*s* orbital to the phosphorus—platinum bond [138]. The degree of *s* and *d* character of a bond (at the expense of *p* character) is believed to give a measure of bond strength [139,140]. Thus a ligand with high *trans* influence will attract a high platinum *s* and *d* bonding contribution, and the resultant decrease in this contribution to the *trans* phosphine—metal bond will be accompanied by reduction of ^1J(Pt—P). Here again, the order of increasing coupling shows the negligible *trans* influence of nitrate: $Me \ll R_3P < CN < Et_3As < \text{amine} \approx N_3 < NCO < NCS < Cl, Br, I < NO_3$. Similar results have been obtained from the complexes *cis*[PtMeX(Et$_3$P)$_2$] (ref. 138).

This high platinum—phosphorus coupling constant induced by nitrate has been found useful in assigning the ^{31}P NMR resonances of the complex [PtMe(NO$_3$)(Ph$_2$P(CH$_2$)$_2$PPh$_2$)] (XII) [141] from which absolute values for ^3J(H—P$_{trans}$) and ^3J(H—P$_{cis}$) have been determined.



(XII)

Studies of ^1J(Pt—P) in *cis*[PtX$_2$(Bu$_3$P)$_2$] showed the same trend to highest coupling and poorest *trans* influence for X = NO_3. In the similar series of *trans* complexes essentially the same order was obtained [142]. Thus NO_3

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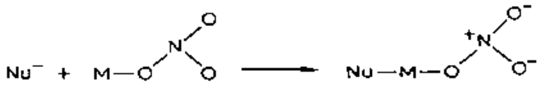
* ν(Pt—H) can only be used in an interpretation of bond strength if no coupling occurs. Existing results suggest that coupling is unlikely [136].

was found to exert lowest *cis* influence. However, an inverse relationship was found for the complexes *cis* and *trans*$[PtX(SCF_3)(PEt_3)_2]$ from ^3J(Pt—F) [143], attributing high *cis* influence to nitrate. This is in contrast to the calculation by Drago and Zumdahl [136] which predicted a trend similar to that of *trans* influence.

^{13}C NMR studies of *trans*-$[PtX(CO)(PPh_3)_2]^+$, containing ^{13}C enriched carbonyl, suggest a similarly low *trans* influence for nitrate [139] by exhibiting the highest ^1J(Pt—C) for the nitrato complex.

F. THE LEAVING GROUP PROPERTY OF NITRATE BOUND TO THE PLATINUM METALS

The strong inductive effect ascribed to nitrate, and the consequent polarity in the metal—nitrate bond, renders nitrato complexes susceptible to nucleophilic attack, the $(x + 1)$ coordinated intermediate of an S_N2 mechanism being stabilised by the ability of the ligand to hold negative charge (x = ground state coordination number) (eqn. (1)). Thus nitrate should exhibit good leaving group properties. Russian workers [97,98,144,180] have extensively examined the hydrolysis of platinum(IV) hexacoordinated ammine-nitrato complexes by conductimetric or potentiometric methods. In all cases nitrate was relatively unstable, equilibrium positions for reactions of the type



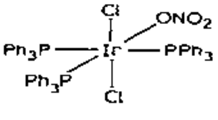
(1)

$$[Pt(NH_3)_2(NO_3)Cl_2(OH)] + H_2O \rightarrow [Pt(NH_3)_2(H_2O)Cl_2(OH)]^+ + (NO_3)^-$$

lying far to the right.

Contrary to expectation, the presence of a ligand with poor *trans* effect in a position *trans* to nitrate has been shown to increase the leaving tendency of the ligand [1,97] in these complexes, suggesting that the reaction may not proceed via a simple '*trans* effect mechanism'. However, all the *trans* ligands examined were of the 'classical' type, owing their position in the *trans* effect series to their polarisability rather than to π-acidity. A ligand that is not easily polarised (i.e. a 'classical' ligand that exerts a poor *trans* influence) often shows a high inductive effect, and would therefore tend to remove electron density from the metal, thus encouraging nucleophilic attack at the metal centre.

Nitrate *trans* to phosphine has been shown to be labile, though in general it appears that the lower (+2) oxidation state platinum metal nitrato complexes may be less susceptible to nucleophilic attack. *Cis*$[Pt(NO_3)_2(PPh_3)_2]$ readily affords the nitrate ion in boiling water [37], and the complex $[IrCl_2(NO_3)(PPh_3)_3]$ (XIII) yields the neutral hydroxo, nitrito, azido or methoxyl species or the cationic ethanol solvate or carbonyl by substitution of nitrate at ambient temperature [72].



(XIII)

The conductivity of solutions of the tetraphenylboron or perchlorate salts of $[Pd(NO_3)(qas)]^+$ (qas = quadridentate arsine ligand, see above) [90] showed an increase in conductivity on the addition of pyridine, attributed to the formation of $[Pd(qas)py]^{2+}$ and $[NO_3]^-$. Similarly, the addition of pyridine or pyridine derivatives, pyrazole or imidazole to a benzene solution of *trans*-$[PdH(NO_3)(Pcy_3)_2]$ (ref. 89) (cy = cyclohexyl) and sodium tetraphenylboron immediately precipitated cationic complexes of the type $[PdH(py)(Pcy_3)_2]^+$-$(BPh_4)^-$.

The high susceptibility of nitrate to solvolysis has been illustrated by conductimetric measurements on the complexes *trans*$[Pt(NO_3)(Ar)(PEt_3)_2]$ (Ar = aryl) [116] in methanol, which show molar conductivities greater than the corresponding chloro derivatives by a factor of ca. 10^2.

A detailed kinetic study of the reactions

$$[M(NH_3)_5(NO_3)]^{2+} + H_2O \rightarrow [M(NH_3)_5(H_2O)]^{3+} + NO_3^- \qquad (2)$$

and

$$[M(NH_3)_5(NO_3)]^{2+} + OH^- \rightarrow [M(NH_3)_5(OH)]^{2+} + NO_3^- \qquad (3)$$

(M = rhodium or iridium) [54], have indicated a dissociative mechanism for the former, and either a unimolecular or bimolecular nucleophilic substitution of H_2O into the conjugate base $[M(NH_3)_4(NH_2)(NO_3)]^+$ for the latter.

The value of nitrate as a leaving group in metallation reactions has been mentioned in Section C, (vi), and its role in metal—hydride insertion reactions is considered in the following section.

G. THE ROLE OF NITRATE IN INSERTION REACTIONS

The "insertion" of an olefin into a metal—hydride bond is thought to be one of the key steps in the catalytic addition of hydrogen to an unsaturated bond. The insertion of ethylene into the platinum—hydrogen bond was first noted for the complex *trans*$[PtHCl(PEt_3)_2]$ by Chatt and Shaw [109], yielding *trans*-$[Pt(C_2H_5)Cl(PEt_3)_2]$ under relatively extreme conditions (368 K, 40 atmospheres in cyclohexane). By replacing chloride with nitrate, however, it has been shown that the ease of insertion can be considerably increased. For example, *trans*$[PtH(NO_3)(PPh_2Me)_2]$ forms the *trans* alkyl$[Pt(C_2H_5)(NO_3)$-$(PPh_2Me)_2]$ (refs. 112,145) by insertion with ethylene at room temperature, whereas insertion into the chloro complex required considerably more drastic treatment, and in the case of the bromo derivative reaction could not be induced. These results imply a relationship between the leaving group property of the anionic ligand and the ease of insertion, and have led to the suggestion that the initial step might involve replacement of that ligand by the π-bonded alkene, forming a four coordinate cationic intermediate. An alternative mechanism via a five coordinate intermediate has also been put forward [146]. Insertion into hydrido—chloro complexes is known to be catalysed by tin(II) chloride, and from this type of reaction a five coordinate intermediate has been isolated. On the other hand, reaction of *trans*$[PtH(NO_3)(PEt_3)_2]$ with ethylene has precipitated *trans*$[PtH(C_2H_4)(PEt_3)_2]^+(BPh_4)^-$ [148,149] by the addition of sodium tetraphenylboron to the methanolic solution, providing good evidence for the four coordinate cationic species. At slightly higher temperatures, in the absence of the sodium salt, the expected alkyl, *trans*$[Pt(C_2H_5)(NO_3)(PEt_3)_2]$, was formed.

A detailed kinetic study [150] of the insertion of methyl acrylate into *trans*$[PtH(NO_3)(PEt_3)_2]$ has suggested a mechanism involving a four coordinate intermediate to be the more probable in the non-catalytic reaction, particularly where a good leaving group is involved [151], the most acceptable mechanism being the scheme shown in eqns. (4)—(6).

$$[PtH(NO_3)(PEt_3)_2] + Z \rightleftharpoons [PtHZ(PEt_3)_2]^+ + (NO_3)^- \tag{4}$$

$$[PtHZ(PEt_3)_2]^+ \rightleftharpoons [PtR(PEt_3)_2]^+ \tag{5}$$

$$[PtR(PEt_3)_2]^+ + (NO_3)^- \rightleftharpoons [PtR(NO_3)(PEt_3)_2] \tag{6}$$

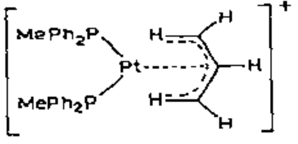
where $Z = CH_2{:}CHCO_2Me$ and $R = CH_3CHCO_2Me$. Investigation of the insertion of ethylene into the platinum—hydrogen bond of *trans*[PtH(acetone)-$(PEt_3)_2]^+$ favours a similar mechanism [151], although studies of these and related systems have been unable totally to discount an intermediate five coordinate state in these uncatalysed insertions [152].

In the favoured four coordinate intermediate system a *cis/trans* isomerism must presumably occur prior to insertion, following the alkyl substitution *trans* to hydride. Indeed, reactions culminating in chelation of a bidentate alkyl following insertion are found to proceed smoothly to the *cis* complex [153,159] (reactions (7) and (8)).

trans$[PtH(NO_3)(PPh_2Me)_2] + (CH_2{:}CHCH_2)_2O$

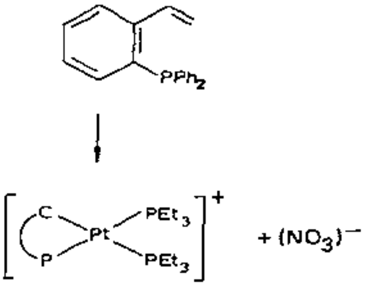
$$\big\downarrow \quad [\text{or} + 2\ CH_2{:}CHCH_2OH]$$

CH_3CH_2CHO +



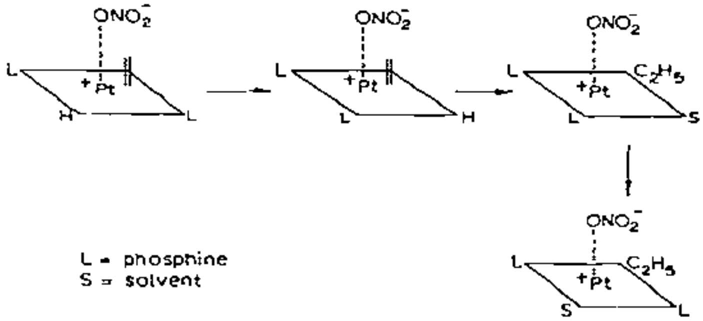
$+ (NO_3)^-$ (7)

trans$[PtH(NO_3)(PEt_3)_2]$ +



(8)

Clark et al. [152] have suggested that the nitrate ion may assist the *cis/trans* isomerism by temporarily 'coordinating' to the axial position of the square planar cation (eqn. (9)).



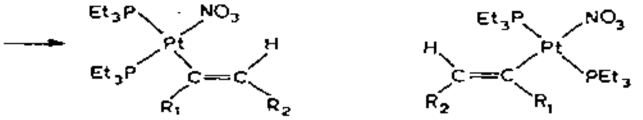
L = phosphine
S = solvent

(9)

Studies of the insertion of substituted acetylenes [124] (see eqn. (10)) consistently found *cis* geometry about the alkenyl (again pointing to a *cis/trans* isomerism before hydrogen transfer to the carbon atom, in a four-centred transition state), and noted that overall *cis* geometry was favoured by electron withdrawing groups, R_1 and R_2, by non-polar solvent, and by substituting chloride with nitrate.

trans$[PtH(NO_3)(PEt_3)_2] + R_1{-}C{\equiv}C{-}R_2 \xrightarrow{\text{(acetone)}}$

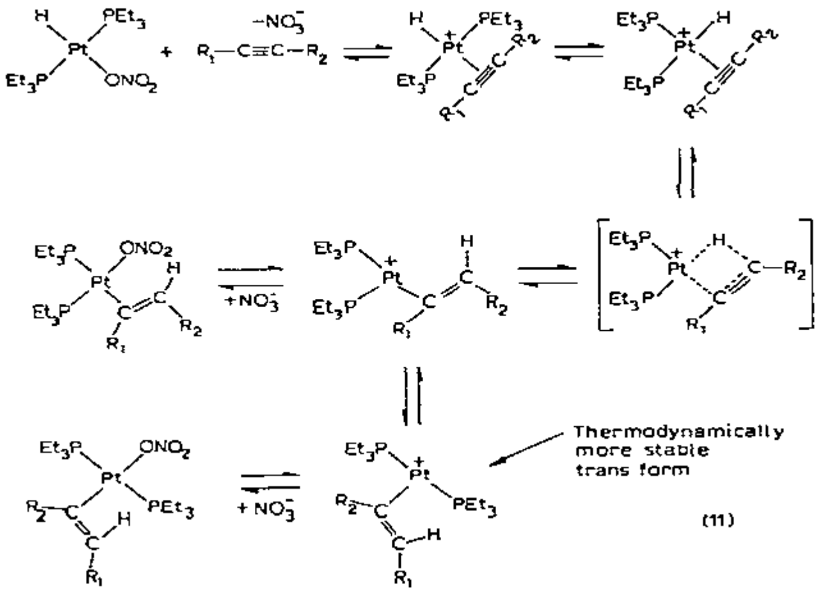
either *cis* or *trans*



(10)

These observations can be acceptably explained by the scheme outlined below [124].

Attack of the three coordinate cation (scheme (11)) would tend to be faster in non-polar solvents, or if the positive charge held by the metal was increased by the presence of electron withdrawing alkyl substituents, so that the kinetically controlled *cis* form would be the major product. However, relative to the chloride, the good leaving group property of nitrate would encourage a more



(11)

rapid equilibration to the thermodynamically more stable *trans* form. The *trans* form is favoured still more if nitrate is replaced by the very weakly coordinating acetone solvent molecule.

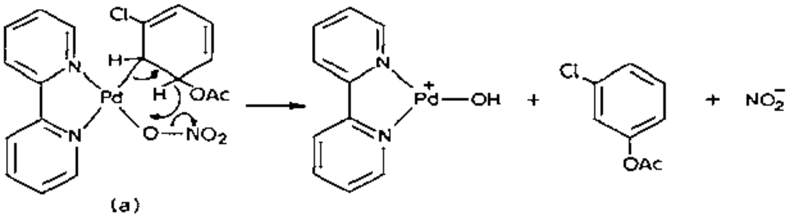
The role of nitrate in metal—carbon insertion reactions has been less thoroughly investigated, though *cis*-[Pt(CH$_3$)(NO$_3$)(LL)] (where LL = the bidentate phosphine, 1,2-phenylenebis(dimethylphosphine)) is known to readily insert R—C≡C—R (R = CF$_3$ or CO$_2$CH$_3$) at ambient temperature to form *cis*-[Pt(RC:CRCH$_3$)(NO$_3$)(LL)] (ref. 118). As in the case of the hydride, *cis* geometry about the alkenyl bond is found, suggesting a similar four-centred insertion mechanism.

H. PLATINUM METAL NITRATO COMPLEXES AS CATALYSTS

Trans[PtH(NO$_3$)(PPh$_2$Me)$_2$] catalyses the controlled oxidation of (CH$_2$:CH-CH$_2$)$_2$O to propaldehyde [154], most probably via the hydrido insertion product discussed in section (b) above [153].

[Pd(MeCO$_2$)(NO$_3$)(2,2'bipyridyl)] has been found to catalyse the acetoxylation of chlorobenzene [80]. The leaving group tendency of nitrate may enhance the initial π-bonding of the chlorobenzene, which will then undergo a form of insertion reaction with the acetoxylate ligand to form the intermediate (a) (eqn. (12)). It has been proposed that nitrate then enhances regeneration of the nitrato—acetato complex via the postulated electron transfer of eqn. (12).

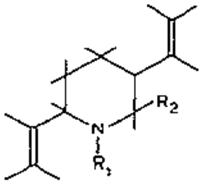
Palladium(II) nitrate and triphenylphosphine, in the molar ratio 1 : 3, have been shown to catalyse the reaction of a Schiff base with 1,3-butadiene to yield a vinyl-substituted piperidine (eqn. (13)). Chloride and acetylacetonate



(12)

salts have proved ineffective in catalysing this reaction [155].

$2\ CH_2{:}CHCH{:}CH_2 + R^1N{:}CHR^2 \longrightarrow$



(13)

(R^1 and R^2 = alkyl)

In acetic acid solution, palladium(II) nitrate has been shown to catalyse reaction with allene affording various unsaturated acetic esters [156]. Here, however, other simple palladium(II) salts show similar activity. In the presence of an equimolar quantity of triphenylphosphine allene polymerisation occurs [156].

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