$(EDDA)CO_3^-$ (EDDA ≡ ethylenediaminediacetic acid) are also available.[22,23]

(22) T. P. Dasgupta and G. M. Harris, *Inorg. Chem.*, **13**, 1275 (1974).

(23) R. van Eldik, T. P. Dasgupta, and G. M. Harris, *Inorg. Chem.*, **14**, 2573 (1975)).

(24) A rough correlation is possible in terms of either the average p*K* of the amine ligand(s) or the p*K* of the product diaquo complex obtained by decarboxylation.[9]

(25) This possibility was suggested tentatively but not supported experimentally in the study by Francis and Jordan.[9]

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Complexes of the Platinum Metals. 14.[1] Nitrato Derivatives of Ruthenium, Osmium, Rhodium, and Iridium

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Nitrato complexes of the platinum group metals have been prepared by treating selected hydridic or zero oxidation state precursors with nitric acid, neat or in organic media. Products obtained in this manner include $[M(NO_3)_2(CO)(PPh_3)_2]$, $[M(NO_3)_2(CO)_2(PPh_3)_2]$ (M = Ru or Os), $[M'(NO_3)_3(PPh_3)_2]$, and $[M'(NO_3)_2(NO)(PPh_3)_2]$ (M′ = Rh or Ir). The species $[M(NO_3)_2(CO)(PPh_3)_2]$ undergo carbonylation to yield the dicarbonyls $[M(NO_3)_2(CO)_2(PPh_3)_2]$ and alcoholysis followed by β-elimination to form the hydrides $[MH(NO_3)(CO)(PPh_3)_2]$. The latter products are readily carbonylated to afford the species $[MH(NO_3)(CO)_2(PPh_3)_2]$. The new complexes have been characterized and their stereochemistry has been assigned by reference to spectroscopic data. The complex "$Rh(NO_3)(NO)_2(OPPh_3)_2$" has been reformulated as $[Rh(NO_3)_2(NO)(PPh_3)_2]$. However, one product obtained on treating $[RuH_2(CO)(PPh_3)_3]$ with nitric acid has been tentatively identified as a triphenylphosphine oxide derivative $[Ru(NO_3)_3(NO)(OPPh_3)(PPh_3)]$. The ability of $[Ru(NO_3)_2(CO)(PPh_3)_2]$ to catalyze the dehydrogenation of primary and secondary alcohols is noted.

Introduction

Oxygen donor ligands, with the notable exception of β-diketonate[2] and carboxylate[3] anions, do not feature extensively in the low oxidation state chemistry of the platinum metals and rarely cohabit with ligands of strong π-acceptor character within the same coordination sphere.[4] Nitrate ligands in particular are generally associated with high oxidation state systems involving aqueous or liquid nitrogen oxide solutions and are rarely encountered in low oxidation state complexes containing phosphines, carbon monoxide, or related π-acceptor ligands.[5]

The nitrate anion shows particularly weak Lewis base properties; it is a poor σ donor and has little if any π-acceptor capacity. In addition the high polarity of $M-ONO_2$ bonds, caused by the strong inductive effect of the nitrate anion, facilitates nucleophilic attack on nitrato complexes. For these reasons the nitrate anion is widely regarded as a highly labile ligand of relatively poor coordinating power, particularly toward platinum group metals.[5,6]

However, a few stable complexes of the platinum group metals containing nitrate anions and strong π-acceptor ligands within the same coordination sphere have been reported. Methods of synthesis employed include metathesis using silver nitrate, addition of nitrogen oxides to dioxygen complexes, oxidation of bound nitrosyl or nitrito ligands, and the treatment of hydridic or low oxidation state complexes with nitric acid.[6] The last-mentioned process has been employed in the present work to synthesize a range of new nitrato complexes containing triphenylphosphine ligands.[7]

Our interest in nitrato complexes arises from our earlier work on the closely related perfluorocarboxylato derivatives[8] and reflects the importance of labile oxygen donor ligands in the chemistry of homogeneous platinum metal catalysts.

Experimental Section

Platinum metal salts were supplied by Johnson Matthey Ltd. and were converted into triphenylphosphine complexes by standard literature procedures.[9] Unless otherwise indicated reactions were performed under nitrogen and products were worked up in air. Yields are based on platinum metal content. Analytical results, obtained by the microanalytical laboratory, University College London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Infrared and NMR data, collected using a Perkin-Elmer 457 grating spectrophotometer and a Bruker HFX90 NMR spectrometer, respectively, are recorded in Table II. Mass spectra were obtained using an AEI MS30 mass spectrometer. *Hazard warning*! Ethanol is liable to violent oxidation by concentrated nitric acid; it is therefore important to note that in the present work only dilute (≤6 M) nitric acid was employed in ethanolic media.

Carbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II). Method a. Finely powdered carbonyldihydridotris(triphenylphosphine)ruthenium (0.5 g) was added, portionwise, to vigorously stirred 16 M nitric acid (40 mL) at 273 K and the mixture allowed to stand for 5 min. The resultant yellow viscous oil was separated by decantation, washed successively with water and cold methanol, and then crystallized from dichloromethane–methanol. The required product was filtered off, washed successively with methanol and petroleum ether, and then dried in vacuo as yellow crystals (0.23 g, 54%).

Method b. A suspension of carbonyldihydridotris(triphenylphosphine)ruthenium (0.40 g) in 3 M nitric acid (15 mL) was boiled under reflux for 1 h. The resulting yellow suspension was filtered off and recrystallized from dichloromethane–methanol and then was washed successively with methanol and petroleum ether and dried in vacuo to yield yellow crystals (0.19 g, 56%).

Similarly prepared by method a from carbonyldihydridotris(triphenylphosphine)osmium was **carbonylbis(nitrato)bis(triphenylphosphine)osmium(II)** as yellow crystals (59%).

Carbonylhydridonitratobis(triphenylphosphine)ruthenium(II). A suspension of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.20 g) in 1-propanol (15 mL) and triethylamine (0.5 mL) was boiled under reflux for 15 min. After the mixture was cooled, the precipitated product was filtered off, washed with ethanol and petroleum ether, and then dried in vacuo as white crystals (0.18 g, 98%).

Similarly prepared from carbonylbis(nitrato)bis(triphenylphosphine)osmium was **carbonylhydridonitratobis(triphenylphosphine)osmium(II)** as white crystals (98%).

Similarly prepared from carbonylbis(nitrato)bis(triphenylphosphine)ruthenium in deuteriomethanol with a reaction time of 1.5 h was **carbonyldeuteridonitratobis(triphenylphosphine)ruthenium(II)** (70%).

Dicarbonylbis(nitrato)bis(triphenylphosphine)ruthenium(II). Method a. A suspension of tricarbonylbis(triphenylphosphine)ruthenium (0.50 g) in 6 M nitric acid (15 mL) and ethanol (15 mL) was boiled under reflux for 15 min. The precipitated product was

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Table I. Melting Point[a] and Analytical Data[b]

Product	Mp/°C	% C	% H	% N
$[Ru(NO_3)_2(CO)(PPh_3)_2]$	269–271 d	57.42 (57.12)	3.93 (3.88)	3.79 (3.60)
$[RuH(NO_3)(CO)(PPh_3)_2]$	198–200 d	61.91 (61.90)	4.37 (4.36)	2.01 (1.95)
$[Ru(NO_3)_2(CO)_2(PPh_3)_2]$	180–183 d	56.53 (56.64)	3.47 (3.75)	3.83 (3.48)
$[RuH(NO_3)(CO)_2(PPh_3)_2]$	156–158 d	60.64 (61.28)	4.18 (4.19)	1.80 (1.88)
$[Ru(NO_3)_3(NO)(PPh_3)(OPPh_3)]$	181–182	50.54 (50.41)	3.63 (3.52)	6.49 (6.53)
$[Os(NO_3)_2(CO)(PPh_3)_2]$	193–194 d	50.48 (51.21)	3.74 (3.46)	3.44 (3.23)
$[OsH(NO_3)(CO)(PPh_3)_2]$	168–170 d	55.02 (55.14)	3.88 (3.88)	2.25 (1.74)
$[Os(NO_3)_2(CO)_2(PPh_3)_2]$	205–206 d	50.70 (50.94)	3.52 (3.35)	2.81 (3.13)
$[OsH(NO_3)(CO)_2(PPh_3)_2]$	214–216 d	54.14 (54.73)	3.85 (3.75)	1.74 (1.68)
$[Rh(NO_3)_3(PPh_3)_2]$	191–193 d	52.80 (53.14)	3.75 (3.71)	4.88 (5.16)[c]
$[Rh(NO_3)_2(NO)(PPh_3)_2]$	200–201 d	55.03 (55.32)	3.91 (3.87)	5.27 (5.37)
$[Ir(NO_3)_3(PPh_3)_2]$	180–182 d	48.24 (47.89)	3.77 (3.35)	4.61 (4.65)[d]
$[Ir(NO_3)_2(NO)(PPh_3)_2]$	179–182 d	49.38 (49.65)	3.64 (3.47)	4.22 (4.82)

[a] d = decomposed. [b] Calculated figures in parentheses. [c] % phosphorus: 7.61 (7.61). [d] % phosphorus: 6.57 (6.86).

Table II. Spectroscopic Data for Nitrato Complexes

Product	Color	τ_{MH}[a]	$^2J_{PH}$, Hz	δ_P,[a,b] ppm	ν(MH),[c] cm^{-1}	ν(CO)/ν(NO),[c] cm^{-1}
$[Ru(NO_3)_2(CO)(PPh_3)_2]$	Yellow			46.5 s		1986
$[RuH(NO_3)(CO)(PPh_3)_2]$	White	26.4 t	19.3	42.3 s	2098 w	1928
$[Ru(NO_3)_2(CO)_2(PPh_3)_2]$	White			27.25 s		2012 2068
$[RuH(NO_3)(CO)_2(PPh_3)_2]$	White	13.9 t	18.6	42.25 s	1940 br	1977 br 2058
$[Ru(NO_3)_3(NO)(PPh_3)(OPPh_3)]$	Orange			54.35 s 26.05 s		1918
$[Os(NO_3)_2(CO)(PPh_3)_2]$	Yellow			−0.1 s		1970
$[OsH(NO_3)(CO)(PPh_3)_2]$	White	29.8 t	16.7	24.35 s	2200 w	1920
$[Os(NO_3)_2(CO)_2(PPh_3)_2]$	White			7.05 s		1985 2059
$[OsH(NO_3)(CO)_2(PPh_3)_2]$	White	12.55 t	20.0	15.8 s	1938	1983 2054
$[Rh(NO_3)_3(PPh_3)_2]$	Yellow					
$[Rh(NO_3)_2(NO)(PPh_3)_2]$	Green			18.0 d[d]		1640 br
$[Ir(NO_3)_3(PPh_3)_2]$	Yellow					
$[Ir(NO_3)_2(NO)(PPh_3)_2]$	Green					1580 m

[a] NMR spectra taken in $CDCl_3$ solution. Key: s, singlet; d, doublet; t, triplet. [b] ^{31}P NMR data referenced to external H_3PO_4 in the sense that increasing field is negative. [c] Spectra taken using Nujol mulls; absorptions strong unless otherwise indicated. Key: m, medium; w, weak; br, broad. All spectra show nitrate bands at ca. 1590–1510 and 1282–1225 cm^{-1}; lower frequency nitrate vibrations are masked by triphenylphosphine absorptions. [d] $^1J_{RhP}$ = 117.2 Hz.

filtered off and recrystallized from dichloromethane–ethanol and then was washed with ethanol and petroleum ether and dried in vacuo as white crystals (0.48 g, 85%).

Method b. Carbon monoxide was bubbled through a suspension of carbonylbis(nitrato)bis(triphenylphosphine)ruthenium (0.30 g) in boiling ethanol (40 mL) for 2 h. After the solution was cooled, the resultant crystalline solid was filtered off, washed with ethanol and petroleum ether, and then dried in vacuo as white crystals (0.28 g, 90%).

Similarly prepared by method b from carbonylbis(nitrato)bis(triphenylphosphine)osmium was **dicarbonylbis(nitrato)bis(triphenylphosphine)osmium(II)** (82%).

Dicarbonylbis(nitrato)bis(triphenylphosphine)osmium(II). Powdered dicarbonyldihydridobis(triphenylphosphine)osmium (0.30 g) was added, portionwise, to 16 M nitric acid (15 mL) at ambient temperature, and the mixture was allowed to stand for 5 min. Excess acid was decanted from the resultant off-white solid, which was then washed with water and methanol. After recrystallizing from dichloromethane–methanol, the product was washed with methanol and petroleum ether and then dried in vacuo as white crystals (0.25 g, 72%).

Dicarbonylhydridonitratobis(triphenylphosphine)ruthenium(II). Carbon monoxide was bubbled through a solution of carbonylhydridonitratobis(triphenylphosphine)ruthenium (0.24 g) in benzene (30 mL) at 298 K for $2^1/_2$ h. After removal of the solvent under reduced pressure, the solid residue was recrystallized from dichloromethane–methanol and then was washed with methanol and petroleum ether and dried in vacuo to yield white crystals (0.20 g, 80%).

Similarly prepared from carbonyldeuteridonitratobis(triphenylphosphine)ruthenium, though in an analytically impure state, was **dicarbonyldeuteridonitratobis(triphenylphosphine)ruthenium(II)** as white crystals.

Dicarbonylhydridonitratobis(triphenylphosphine)osmium(II). Carbon monoxide was bubbled through a boiling solution of carbonylhydridonitratobis(triphenylphosphine)osmium (0.2 g) in benzene (30 mL) for 3 h. After removal of the solvent under reduced pressure, the resultant yellow oil was crystallized from dichloromethane–methanol and then was washed with methanol and petroleum ether and dried in vacuo to yield white crystals (0.2 g, 97%).

Tris(nitrato)nitrosyl(triphenylphosphine)(triphenylphosphine oxide)ruthenium(II). Dropwise addition of 16 M nitric acid (1.0 mL) to a solution of carbonyldihydridotris(triphenylphosphine)ruthenium (0.38 g) in benzene (30 mL) produced a deepening in the color of the benzene phase, accompanied by evolution of dihydrogen. After heating of the mixture on a steam bath for 1 h, sufficient sodium bicarbonate was added to neutralize unreacted acid, and the solvent was removed by evaporation under reduced pressure. The residue was extracted with hot methanol (40 mL), and the extract was set aside to crystallize. The product, which deposited from the extract over a period of 2 days, was filtered off, washed with methanol and petroleum ether, and dried in vacuo as orange crystals (0.20 g, 56%).

The complex was similarly prepared from acetatohydridotris(triphenylphosphine)ruthenium (yield 31%).

Tris(nitrato)bis(triphenylphosphine)rhodium(III). Sixteen molar nitric acid (1 mL) was added, dropwise, to a stirred solution of carbonylhydridotris(triphenylphosphine)rhodium (0.30 g) in benzene (30 mL) or chloroform (30 mL). The mixture was evaporated to dryness on a steam bath, the transient green coloration giving way to yellow within 2 min of heating. The required product was extracted with dichloromethane (20 mL) and, after addition of methanol and setting aside, was obtained as yellow crystals, which were washed with methanol and petroleum ether and dried in vacuo; yield 0.21 g, 79%.

Similarly prepared from carbonylhydridotris(triphenylphosphine)iridium was **tris(nitrato)bis(triphenylphosphine)iridium(III)** as yellow crystals (89%).

Reaction of Tris(nitrato)bis(triphenylphosphine)rhodium with Carbon Monoxide. Carbon monoxide was bubbled through a suspension of tris(nitrato)bis(triphenylphosphine)rhodium (0.4 g) in boiling benzene (20 mL) for 3 h, and the resultant yellow solution was set aside to crystallize. The product was filtered off, recrystallized from dichloromethane–methanol, washed with methanol and then petroleum ether, and dried in vacuo as yellow crystals (0.24 g).

Bis(nitrato)nitrosylbis(triphenylphosphine)rhodium(III). Method a. A suspension of nitrosyltris(triphenylphosphine)rhodium (0.20 g) in a mixture of 4 M nitric acid (15 mL) and ethanol (15 mL) was gently heated in an apparatus open to the air for 30 min. After the mixture was cooled, the required product was filtered off and recrystallized from dichloromethane–methanol and then was washed with methanol and petroleum ether and dried in vacuo as green crystals (0.13 g, 76%).

Method b. Powdered carbonylhydridotris(triphenylphosphine)rhodium (0.25 g) was added, portionwise, to vigorously stirred 16 M nitric acid (25 mL). Excess acid was decanted from the resultant viscous green oil, which was then washed with water and methanol, dissolved in a 1/1 (v/v) mixture of dichloromethane and methanol, and set aside to crystallize. The required product was obtained as green crystals, which were filtered off, washed with methanol and then petroleum ether, and dried in vacuo; yield 0.20 g, 94%.

Similarly prepared by method a from nitrosyltris(triphenylphosphine)iridium or from carbonylnitrosylbis(triphenylphosphine)iridium was **bis(nitrato)nitrosylbis(triphenylphosphine)iridium(III)** as pale green crystals (64% and 59%, respectively).

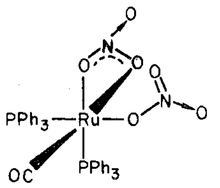
Reaction of Bis(nitrato)nitrosylbis(triphenylphosphine)rhodium with Hydrogen Chloride. Dry hydrogen chloride gas was bubbled through a suspension of bis(nitrato)nitrosylbis(triphenylphosphine)rhodium (0.20 g) in benzene (30 mL) at ambient temperature for 10 min. The resultant orange solution was set aside to crystallize. The product was filtered off, washed with methanol and petroleum ether, and dried in vacuo as orange crystals (0.12 g). The infrared spectrum showed the product to be identical with an authentic sample of **dichloronitrosylbis(triphenylphosphine)rhodium(III).**

Results and Discussion

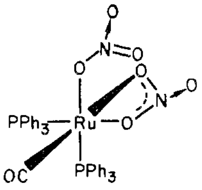
$[M(NO_3)_2(CO)(PPh_3)_2]$ (M = Ru or Os). These air-stable yellow crystalline products, prepared by the action of 16 M (i.e., concentrated) nitric acid at 273 K on the solid dihydrides $[MH_2(CO)(PPh_3)_3]$, were obtained in relatively low yield (50–60%) because of the simultaneous formation of nitrosyl-containing by-products (see later). Assuming the adoption of six-coordination by ruthenium(II) and osmium(II), the stoichiometry $[M(NO_3)_2(CO)(PPh_3)_2]$ implies the presence of one unidentate and one bidentate nitrate ligand in each complex. This situation gives rise to six possible isomers.

The ^{31}P NMR spectrum (298 K) of each complex consists of a singlet which decoalesces to an AB pattern on cooling below ca. 180 K. This behavior is analogous to that observed for the corresponding trifluoroacetates $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$[8] and is indicative of a fluxional system involving interchange of monodentate and bidentate nitrate ligands. Examination of the six possible stereochemical arrangements for the complexes $[M(NO_3)_2(CO)(PPh_3)_2]$ establishes that only a rapid interconversion of configurations Ia and Ib is compatible with the spectroscopic data. Kinetic studies by dynamic NMR spectroscopy have shown[10] that this process occurs by interchange of mono- and bidentate nitrate ligands either via an intermediate (Ic) or, at higher temperatures, by direct interchange (Ia $\rightleftharpoons$ Ib).

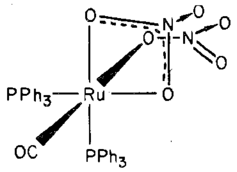
Like its perfluorocarboxylato analogues,[11] the ruthenium complex catalytically dehydrogenates alcohols to aldehydes, presumably by a similar β-elimination mechanism.[12]



Ia



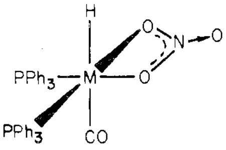
Ib



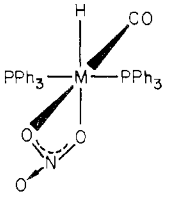
Ic

$[MH(NO_3)(CO)(PPh_3)_2]$. These air-stable white crystalline products were obtained in high yield by the alcoholysis of the complexes $[M(NO_3)_2(CO)(PPh_3)_2]$. For the preparation of the ruthenium complex in boiling ethanol a reaction time of ca. 1.5 h was required for complete reaction, whereas in 1-propanol, which has a boiling point 19 °C above that of ethanol, ca. 30 min was sufficient. However, these reaction times were considerably reduced by the presence of excess triphenylphosphine (30 min for ethanol and ca. 10 min for 1-propanol). A similar acceleration was encountered in the presence of excess triethylamine, suggesting the basic nature rather than the coordinating ability of the excess reagent to be the important factor. Similar behavior was observed in the preparation of the osmium derivative.

The temperature-independent NMR spectra (298 K) show, for each complex, one high-field ^1H triplet which, together with one ^{31}P singlet (M = Ru, δ = 42.3 ppm; M = Os, δ = 24.35 ppm), indicates the presence of two magnetically equivalent ^{31}P nuclei. This condition is satisfied by both configurations IIa and IIb. The relatively high values of the hydride resonances (M = Ru, τ_{MH} 26.4; M = Os, τ_{MH} 29.8) and of the M–H infrared stretching frequencies (ν(RuH) 2098 cm^{-1}, ν(OsH) 2200 cm^{-1}) suggest that the proton is trans to a poor σ donor with weak trans influence. Thus, structure IIb is favored.



IIa

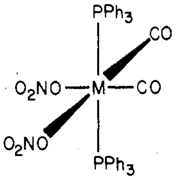


IIb

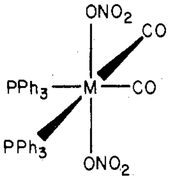
On treatment with 6 M nitric acid the hydrido complexes regenerate the parent species $[M(NO_3)_2(CO)(PPh_3)_2]$. Although this is not a particularly convenient preparative route to the dinitrates, the reaction does point to the possibility of generating a catalytic cycle in which the alcoholic solvent is dehydrogenated, and this has now been demonstrated.[12]

$[M(NO_3)_2(CO)_2(PPh_3)_2]$. These white air-stable crystalline products were obtained in high yield by the action of nitric acid on the polycarbonyls $[Ru(CO)_3(PPh_3)_2]$ and $[OsH_2(CO)_2(PPh_3)_2]$. Although treatment with boiling dilute ethanolic nitric acid (3 M) was sufficient in the case of the ruthenium complex, the less reactive osmium precursor required heating in 16 M nitric acid before reaction was achieved. The complexes have also been obtained as by-products in low yield (less than 10%) from the reaction of benzene or chloroform solutions of the dihydrides $[MH_2(CO)(PPh_3)_3]$ with 16 M nitric acid. The excess carbon monoxide is presumably derived from the primary reaction, in which the precursor is decarbonylated to a nitrosyl–nitrato product (see later). Finally the complexes have been obtained by the action of carbon monoxide on the monocarbonyls $[M(NO_3)_2(CO)(PPh_3)_2]$. ^{31}P NMR (298 K) spectra show one singlet for each complex (M = Ru, δ = 27.25 ppm; M = Os, δ = 7.05 ppm), and infrared spectra each exhibit two very strong absorptions (M = Ru, 2012, 2068 cm^{-1}; M = Os, 1985, 2059 cm^{-1}) attributable to carbonyl.

Of the five possible stereochemical arrangements for the complexes $[M(NO_3)_2(CO)_2(PPh_3)_2]$, only two (IIIa and b) are compatible with the spectroscopic data. However, in the absence of an X-ray diffraction study it is difficult to conclusively assign either one of these configurations to the complexes. A similar difficulty has been encountered for the cis dicarbonyl species $[RuCl_2(CO)_2(PPh_3)_2]$, which has been obtained in two isomeric forms. The more stable of these, isomer A, has been separately assigned stereochemistry IIIa[13] and IIIb[14] (NO_3 becomes Cl) on the basis of ^1H NMR and dipole moment evidence. Configuration IIIa has also been ascribed to the less stable isomer, B, on the basis of infrared evidence[15]. However, ^{13}C NMR has now confirmed that isomer A exhibits stereochemistry IIIa[16] and thus isomer B is probably IIIb.[17] Comparison of the infrared absorption frequencies of the cis dicarbonyls $[RuCl_2(CO)_2(PPh_3)_2]$ (isomer A, ν(CO) 2064, 2001 cm^{-1}; isomer B, ν(CO) 2042, 1967 cm^{-1}) and $[Ru(NO_3)_2(CO)_2(PPh_3)_2]$ (ν(CO) 2068, 2012 cm^{-1}) thus favors stereochemistry IIIa for the latter, since similar trans influence would be expected from either chloride or nitrate trans to carbonyl. Although ^{31}P coupled carbonyl ^{13}C NMR could potentially differentiate between these structures (IIIa giving rise to one triplet, IIIb to a doublet of doublets), the poor solubility of the complexes in suitable solents prevented the high concentrations required by this technique from being obtained.



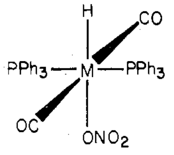
IIIa



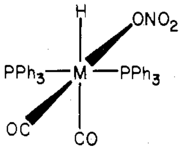
IIIb

$[MH(NO_3)(CO)_2(PPh_3)_2]$. These white crystalline products were obtained by the action of carbon monoxide on a benzene solution of the hydrides $[MH(NO_3)(CO)(PPh_3)_2]$. The ruthenium complex required a carefully controlled reaction time at ambient temperature in order to avoid further carbonylation to the zero oxidation state complex $[Ru(CO)_3(PPh_3)_2]$; however, no such reduction was observed in the case of osmium even in boiling benzene.

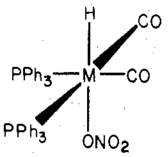
Three absorptions, one attributable to ν(MH) and two to ν(CO) (M = Ru, 1940, 1977, 2058 cm^{-1}; M = Os, 1938, 1983, 2054 cm^{-1}), are observed in the infrared spectra of the products. In addition, both complexes show one ^1H NMR triplet (M = Ru, τ_{MH} 13.9; M = Os, τ_{MH} 12.55) and one ^{31}P singlet (M = Ru, δ = 42.25 ppm; M = Os, δ = 15.8 ppm) indicative of two magnetically equivalent phosphorus nuclei, consistent with configurations IVa–c.



IVa



IVb



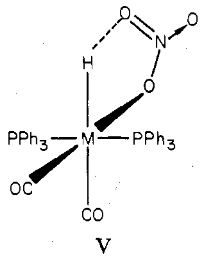
IVc

The presence of two strong infrared frequencies attributable to ν(CO) enables structure IVa to be eliminated. The exceptionally low values of the hydridic NMR resonances reveal a relatively deshielded proton, thus virtually excluding the possibility of hydride trans to nitrate but rather suggesting the removal of electron density by a trans ligand with high π acidity. The strong π-acceptor property of carbonyl therefore indicates stereochemistry IVb. This contrasts with the configuration most recently proposed for the dicarbonyl $[RuHCl(CO)_2(PPh_3)_2]$,[17] which was assigned stereochemistry IVc (nitrate becomes chloride) on the basis of the similarity between the carbonyl infrared frequencies and those of the dicarbonyl $[RuCl_2(CO)_2(PPh_3)_2]$ (isomer B) in which the two anionic ligands are believed to be trans (see above). Here, however, no attempt was made to explain the low τ_{MH} value of 14.5.

Hydride ligands bound to third-row transition metals are usually more highly shielded than those found in analogous complexes of the corresponding second-row metals. The ^1H NMR metal hydride resonance of an osmium hydrido complex is therefore expected at higher field compared to its ruthenium analogue. However, these complexes exhibit a notably lower τ_{MH} value when M = Os. A similar inversion has been noted for the ^1H (hydride) resonances of the analogous trifluoroacetates $[MH(OCOCF_3)(CO)_2(PPh_3)_2]$.[18]

Infrared spectra of the complexes present further difficulties. Within the region 2100–1900 cm^{-1} three strong absorptions are exhibited by each complex, two attributable to ν(CO) of mutually cis carbonyls and one to ν(MH). In view of the considerable bond weakening effect of the trans carbonyl of configuration IVb, ν(MH) has been assigned to the lowest of the three frequencies, following similar interpretations for related complexes.[19] In order to test this assignment, a deuterated sample of the ruthenium complex was prepared via $[RuD(NO_3)(CO)(PPh_3)_2]$. The infrared spectrum of the resultant complex showed the two highest frequency absorptions to remain and the low frequency band, formerly at 1940 cm^{-1}, to have disappeared. However, it was not possible to detect the expected new ν(MD) absorption at ca. 1370 cm^{-1} since this region was masked by other bands.

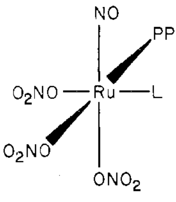
The values of τ_{MH} appear to be inexplicably low even for hydride trans to carbonyl. Hydrides trans to carbonyl in, for example, $[MH_2(CO)_2(PPh_3)_2]$ resonate at $\tau \sim 16.9$ (M = Ru) and at $\tau \sim 17.65$ (M = Os),[20] and hydride trans to carbonyl in $[MH_2(CO)(PPh_3)_3]$ resonates at $\tau \sim 16.5$ (M = Ru) and at $\tau \sim 17.6$ (M = Os).[21] Therefore, the possibility that the hydridic proton may interact in a form of "hydrogen bond"[22] with the uncoordinated oxygen of the unidentate cis nitrate has been considered. Such an interaction (structure V) would be enhanced by the poor σ-donor and strong π-acceptor property of trans carbonyl and would be expected to decrease both τ_{MH} and ν(MH). However, the inversion of τ_{RuH} and τ_{OsH} would imply stronger "hydrogen bonding" within the osmium complex, and an acceptable explanation for this is not apparent. Furthermore, $[RuHCl(CO)_2(PPh_3)_2]$, in which such an intramolecular interaction could not occur, exhibits a similar low τ_{RuH} resonance. Finally, the hydride resonance of the ruthenium nitrato complex has been found to be temperature independent, whereas "hydrogen bonding" would require temperature dependence.



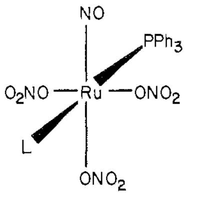
V

$[Ru(NO_3)_3(NO)(PPh_3)(OPPh_3)]$. This air-stable orange crystalline product was obtained by the prolonged action of

16 M nitric acid at ca. 370 K on a benzene solution either of the dihydride $[RuH_2(CO)(PPh_3)_3]$ or of the acetate hydride $[Ru(OCOCH_3)H(PPh_3)_3]$. It was also formed as a by-product in low yield (less than 20%) in the preparation of the species $[Ru(NO_3)_2(CO)(PPh_3)_2]$ from the same precursor but in the absence of a solvent. The yield of this by-product increased when the preparation was carried out at higher temperatures. Attempts to prepare the osmium analogue from $[OsH_2(CO)(PPh_3)_3]$ by a similar method resulted in a deep yellow solid with a strong infrared absorption at ca. 1850 cm^{-1}. However, analytically pure crystals were not isolated. The high infrared absorption at 1918 cm^{-1} for the ruthenium complex is of similar frequency to those observed for the complexes $[RuX_3(NO)(PPh_3)_2]$ (X = Cl, Br, or I).[23] Indeed the complex was initially formulated as $[Ru(NO_3)_3(NO)(PPh_3)_2]$ on the basis of its similarity to these complexes, and to the related $[Ru(OCOCF_3)_3(NO)(PPh_3)_2]$, but analysis figures consistently favored the presence of one extra oxygen atom per molecule. Additional evidence to support reformulation as a phosphine–phosphine oxide complex is provided by both infrared and ^{31}P NMR data. A strong infrared absorption at 1130 cm^{-1} in addition to the expected triphenylphosphine band at ca. 1100 cm^{-1} could be assigned as $\nu(P{=}O)$ of phosphine oxide[24] shifted to lower frequency on coordination. The ^{31}P NMR spectrum (298 K) shows two singlets of equal integral intensity, with no evidence of phosphorus–phosphorus coupling. This is indicative either of equimolar quantities of two isomers, each with equivalent phosphines (structures VIa and VIb, L = PPh_3), or of one complex containing nonequivalent phosphorus nuclei between which there is negligible coupling.



VIa



VIb

The former possibility is considered to be unlikely, since separation attempts result in the same 1:1 integrated intensity relationship. The presence of one triphenylphosphine oxide ligand eliminates the possibility of phosphorus–phosphorus coupling and thus renders ^{31}P NMR data useless in making a stereochemical assignment. However, by analogy with the complex $[Ru(NO)Cl_3(PPh_2Me)_2]$, for which X-ray[25] and ^{1}H NMR studies[26] have revealed a trans disposition of the phosphines, configuration VIb (L = $OPPh_3$) is preferred.

$[M'(NO_3)_3(PPh_3)_2]$ (M' = Rh or Ir). These intractable air-stable yellow crystalline products were obtained by the action of 16 M nitric acid on benzene or chloroform solutions of the hydrides $[M'H(CO)(PPh_3)_3]$. A transient green coloration suggests that the complexes may be formed via the corresponding nitrosyl intermediates $[M'(NO_3)_2(NO)(PPh_3)_2]$ (see below). Certainly these tris(nitrates) are obtained by the action of 16 M nitric acid on the complexes $[M'(NO_3)_2(NO)(PPh_3)_2]$ in benzene solution.

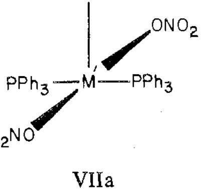
The very low solubility of the complexes $[M'(NO_3)_3(PPh_3)_2]$ in all common solvents greatly hindered their full characterization, and we cannot exclude the possibility that they may be polynuclear.

Treatment of the rhodium complex in benzene with carbon monoxide afforded yellow crystals. Carbonyl, nitrate, and triphenylphosphine bands were identified in the infrared spectrum of the product, but we were unable to positively establish its stoichiometry. Consistent with the generally lower lability of iridium complexes, $[Ir(NO_3)_3(PPh_3)_2]$ showed no reaction under similar conditions.

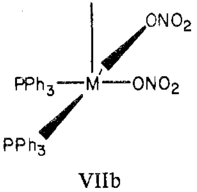
$[M'(NO_3)_2(NO)(PPh_3)_2]$. These air-stable green crystalline products, obtained by the action of 2 M ethanolic nitric acid on the corresponding metal nitrosyl complexes $[M'(NO)(PPh_3)_3]$, probably also account for the transient green coloration observed during the preparation of the species $[M'(NO_3)_3(PPh_3)_2]$. Attempts to prepare the rhodium complex in degassed solvents under anaerobic conditions gave no reaction.[27] Introduction of a stoichiometric amount of dioxygen [Rh:O_2 ratio 1:1] induced complete precipitation of the nitrosyl nitrate within 30 min; smaller quantities of dioxygen brought about incomplete reaction. Thus, it appears that the role of dioxygen is stoichiometric rather than catalytic. A similar dioxygen dependence has been previously observed in the preparation of $[Rh(OCOCF_3)_2(NO)(PPh_3)_2]$ from the same precursor,[28] and for this reaction, mechanisms involving a hydroperoxy intermediate (protonation followed by addition and insertion of dioxygen) are currently being examined.[27]

Reactions of $[Rh(NO)(PPh_3)_3]$ with a number of other acids (for example, acetic, benzoic, methanesulfonic, and trifluoromethanesulfonic acids) have recently been shown similarly to require molar proportions of dioxygen.[27] In this context it is interesting to note that osmometric molecular weight determinations for the precursor, $[Rh(NO)(PPh_3)_3]$, indicate that a high degree of dissociation only occurs in the presence of air.[29] $[Ir(NO)(PPh_3)_3]$ shows no such air sensitivity, and synthesis of $[Ir(NO_3)_2(NO)(PPh_3)_2]$ from this complex shows no dioxygen requirement.

The rhodium complex was also prepared by the direct reaction of solid $[RhH(CO)(PPh_3)_3]$ with neat (16 M) nitric acid and is identical with the complex "$Rh(NO)_2(NO_3)(OPPh_3)_2$", previously obtained by treating $[RhH(PPh_3)_4]$ with dilute nitric acid.[30] In particular, the infrared spectra of our complex [$\nu(NO)$ 1640 cm^{-1}, $\nu(NO_3)$ 1540, 1512, 1270, 985 cm^{-1}] correspond well with that recorded for "$Rh(NO)_2(NO_3)(OPPh_3)_2$" [$\nu(NO)$ 1645 cm^{-1}, $\nu(NO_3)$ 1539, 1512, 1271, 985 cm^{-1}].[30] The complex also appears identical in color and in infrared frequencies to the complex "$Rh(NO)(NO_3)(PPh_3)_2$", obtained by treating $[Rh(NO_2)(CO)(PPh_3)_2]$ with concentrated nitric acid.[31] The relatively low infrared absorptions attributable to nitrosyl [M' = Rh, $\nu(NO)$ 1640 cm^{-1}; M' = Ir, $\nu(NO)$ 1580 cm^{-1}] indicate the presence of a nonlinear M–N–O moiety, thereby suggesting that the complexes $[M'(NO_3)_2(NO)(PPh_3)_2]$ are formal derivatives of Rh(III) and Ir(III), analogous to the well-known halides $[M'X_2(NO)(PPh_3)_2]$. The poor solubility of both complexes in suitable solvents has rendered ^{31}P NMR data difficult to obtain. However, the apparent ^{31}P doublet of the rhodium complex [centered at δ = 18.0 ppm, $^{1}J_{RhP}$ = 117 Hz], indicative of magnetically equivalent phosphorus nuclei, suggests trans or cis square-pyramidal configurations VIIa or VIIb.



VIIa



VIIb

Alternative trigonal-bipyramidal structures involving axial or equatorial nonlinear nitrosyl groups are also consistent with the spectroscopic data but are discounted on theoretical grounds.[32] Finally, since the corresponding dichlorides $[M'Cl_2(NO)(PPh_3)_2]$ both display square-pyramidal structures with trans phosphine ligands,[33,34] the weight of evidence clearly favors stereochemistry VIIa.

The dark green rhodium complex was previously formulated as "$Rh(NO)_2(NO_3)(OPPh_3)_2$" on the basis of mass spectra and infrared evidence.[30] The fragmentation mass spectrum was found to contain a high abundance of $(Ph_3PO)^+$ ions, and the presence of a strong infrared absorption at 1098 cm^{-1} was attributed to ν(P=O) of coordinated phosphine oxide.

A mass spectrum was taken of our sample of the rhodium complex, and peaks attributable both to triphenylphosphine and to triphenylphosphine oxide were certainly obtained in approximately equal weight. Although occurrence of triphenylphosphine oxide parent ions and fragmentation products in the mass spectrum is obviously consistent with the presence of triphenylphosphine oxide ligands, it is open to other interpretations. These species could equally well be generated in the high-energy environment of the spectrometer itself, by interaction of triphenylphosphine either with nitrate ions (the latter are known to oxidize other ligands at high energy)[35] or with traces of dioxygen. Alternatively, they may be derived from trace impurities of phosphine oxide derivatives within the sample. In the light of the relatively poor coordinating power of this ligand toward the platinum group metals, such an impurity would be expected to volatilize more efficiently to give a spectrum disproportionately high in the oxide. Since we have observed similarly high phosphine oxide peaks in the mass spectrum of the known complex $[Rh(NO)Cl_2(PPh_3)_2]$, the last two interpretations would seem most probable. The infrared evidence is similarly inconclusive. Triphenylphosphine oxide displays a strong band at 1200 cm^{-1} [ν(P=O)][24] that moves to lower frequency on coordination. However, the band at 1098 cm^{-1} observed in the infrared spectrum of the rhodium nitrate complex is substantially below the frequency range normally associated with the ν(P=O) vibrations in group 8 metal triphenylphosphine oxide complexes[36] and is apparently coincident with a region in which bound triphenylphosphine and triphenylphosphine oxide both absorb strongly. A comparison of this rhodium complex with the perfluorocarboxylato derivatives $[Rh(OCOR_F)_2(NO)(PPh_3)_2]$,[28] for which triphenylphosphine oxide fomulations are excluded by analytical data, shows that both nitrato and perfluorocarboxylato complexes have very similar ultraviolet and visible spectra and all display rhodium–phosphorus NMR couplings [$^1J_{RhP}$ = ca. 120 Hz] indicative of a direct Rh–P linkage.[37] Furthermore, the nitrato complex reacts efficiently with hydrogen chloride to generate the known dichloride $[RhCl_2(NO)(PPh_3)_2]$ which has also been shown by ^{31}P NMR to contain direct Rh–P bonding.[38]

Registry No. $Ru(NO_3)_2(CO)(PPh_3)_2$, 66255-67-2; $RuH(NO_3)(CO)(PPh_3)_2$, 66255-84-3; $Ru(NO_3)_2(CO)_2(PPh_3)_2$, 66289-72-3; $RuH(NO_3)(CO)_2(PPh_3)_2$, 66255-83-2; $Ru(NO_3)_3(NO)(PPh_3)(OPPh_3)$, 66255-82-1; $Os(NO_3)_2(CO)(PPh_3)_2$, 66255-81-0; $OsH(NO_3)(CO)(PPh_3)_2$, 66255-80-9; $Os(NO_3)_2(CO)_2(PPh_3)_2$, 66289-71-2; $OsH(NO_3)(CO)_2(PPh_3)_2$, 66289-70-1; $Rh(NO_3)_3(PPh_3)_2$, 60284-35-7; $Rh(NO_3)_2(NO)(PPh_3)_2$, 66289-69-8; $Ir(NO_3)_3(PPh_3)_2$, 60284-37-9; $Ir(NO_3)_2(NO)(PPh_3)_2$, 66289-68-7; $RuH_2(CO)(PPh_3)_3$, 25360-32-1; $OsH_2(CO)(PPh_3)_3$, 12104-84-6; $RuD(NO_3)(CO)(PPh_3)_2$, 66255-79-6; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $OsH_2(CO)_2(PPh_3)_2$, 18974-23-7; $RuD(NO_3)(CO)_2(PPh_3)_2$, 66255-78-5; $RuH(O_2CMe)(PPh_3)_3$, 55354-87-5; $RhH(CO)(PPh_3)_3$, 17185-29-4; $IrH(CO)(PPh_3)_3$, 17250-25-8; $Rh(NO)(PPh_3)_3$, 21558-94-1; $Ir(NO)(PPh_3)_3$, 25448-15-1; $Ir(CO)(NO)(PPh_3)_2$, 30919-43-8; CO, 630-08-0.

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