Structural and Spectroscopic Studies of Rhodium-(I) and -(III) Nitrato Complexes†

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Refluxing $Rh(NO_3)_3{\cdot}2H_2O$ with an excess of PPh_3 in MeOH or EtOH for over 48 h gives *trans*-$[Rh(CO)(ONO_2)(PPh_3)_2]$ **1** whereas the same reaction at room temperature gives predominantly $[Rh(ONO_2)(PPh_3)_3]$ **2**. X-Ray structure determinations of **1** and **2** show the nitrate groups to be monodentate in each case although disorder of the CO and NO_3 groups in **1** precludes accurate determination of bond lengths and angles. There is no reaction of *trans*-$[Rh(CO)X(PPh_3)_2]$ (X = Cl, F or ONO_2) with H_2 at room temperature and 1 atm pressure, whereas there is an immediate reaction of $[Rh(ONO_2)(PPh_3)_3]$ under the same conditions to give $[RhH_2(ONO_2)(PPh_3)_3]$ **3**, which has been characterised by multinuclear NMR spectroscopy. Compound **3** loses PPh_3 to give $[RhH_2(O_2NO)(PPh_3)_2]$ **6a** which has been characterised similarly and by X-ray crystallography; although the metal-bound hydrogens were not located the structure is clearly based on an octahedral geometry with *trans* phosphines and a bidentate nitrate.

The reaction of rhodium trichloride with excess of triphenylphosphine in ethanol to give Wilkinson's compound, $[RhCl(PPh_3)_3]$, has long been known[1] and it has been successfully used commercially as an efficient hydrogenation catalyst.[2] Multinuclear NMR measurements in solution have proved to be very useful in characterising the stereochemistries, reactions and exchange processes of both $[RhCl(PPh_3)_3]$[3,4] and the product resulting on oxidative addition with H_2, *viz.* $[RhH_2Cl(PPh_3)_3]$.[4] This information is extremely important in elucidating the involvement of each of these species and the associated equilibria in the catalytic hydrogenation of alkenes.[4,5] Many other analogues of $[RhCl(PPh_3)_3]$, obtained by replacing chloride with other monovalent groups, have been reported[2] but NMR measurements on these complexes and their related hydrogenated derivatives, $[RhH_2X(PPh_3)_3]$, have been much less extensive, and there are no NMR measurements on either rhodium-(I) or -(III) complexes when X = NO_3.

We now report the preparation, chemical reactivity, structural and spectroscopic characterisation of a series of rhodium nitrato complexes which, although related to Wilkinson's compound and analogous derivatives, do show significant differences.

Results and Discussion

The reaction of $Rh(NO_3)_3{\cdot}2H_2O$ with excess of PPh_3 in refluxing EtOH or MeOH for over 48 h is found to give yellow crystals of *trans*-$[Rh(CO)(ONO_2)(PPh_3)_2]$ **1**. Decarbonylation of alcohols by rhodium is not uncommon but it was a little surprising to obtain *only* **1** from this reaction.

The X-ray analysis of compound **1** showed the NO_3 group to be monodentate but unfortunately disorder of the CO and NO_3 groups, analogous to that found in the triclinic form of *trans*-$[Rh(CO)Cl(PPh_3)_2]$,[6] precluded the accurate determination of bond lengths and angles (see Experimental section). Nevertheless, both ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR data (Tables 1 and 2) are entirely in accord with the formulation of **1**. Thus, the ^{31}P-$\{^1H\}$ NMR spectrum consists of a single doublet at δ 31.2 [^1J(Rh–P) 131 Hz] due to the *trans*-$Rh(PPh_3)_2$ group and ^{13}CO enrichment, by direct exchange with ^{13}CO, caused this resonance to be further split due to ^2J(P–CO) 16.9 Hz. Additionally, there is a single resonance δ 190.9 in the ^{13}C-$\{^1H\}$ NMR spectrum which consists of a doublet [^1J(Rh–CO) 74.7 Hz] of triplets [^2J(P–CO) 16.9 Hz]. However, it should be noted that solutions of **1** in $CDCl_3$ decomposed over a few hours at room temperature and, even at lower temperatures, the above resonances are slowly replaced by a similar set of resonances which we attribute to the formation of *trans*-$[Rh(CO)Cl(PPh_3)_2]$ (Tables 1 and 2). Unfortunately, **1** is only sparingly soluble in non-chlorinated solvents and thus chloride abstraction from the solvent was unavoidable. For comparison, *trans*-$[Rh(CO)F(PPh_3)_2]$ was prepared by the method of Vaska and Peone[7] and the NMR data are reported in Tables 1 and 2.

At room temperature, there is no reaction of *trans*-$[Rh(CO)X(PPh_3)_2]$ (X = F, Cl or ONO_2) with H_2 (1 atm).

In contrast to the above reaction in refluxing MeOH, the analogous reaction of $Rh(NO_3)_3{\cdot}2H_2O$ with excess of PPh_3 (1:15 molar ratio) in MeOH at room temperature follows a completely different course. A small amount of a yellow-green precipitate (see below) was obtained after reaction for 12 h and on filtering this from the red solution only red crystals of $[Rh(ONO_2)(PPh_3)_3]$ **2** were obtained from the filtrate on standing for 3–5 d. The molecular structure of **2** is given in Fig. 1 with selected bond lengths and angles in Table 3. It reveals the usual approximate square-planar geometry around rhodium with a monodentate nitrate group. The arrangement of this group is such that the NO_3 plane makes an angle of 105.7(1)° with the P_3RhO co-ordination plane. The value of angle Rh–O–N (115°) and the distance of 2.936 Å between the metal and the non-co-ordinated oxygen indicates the possibility of some form of interaction, although there is no NMR spectro-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.
Non-SI unit employed: atm = 101 325 Pa.

Table 1 Phosphorus-31 NMR data for rhodium(I) complexes

Compound	Solvent	T/°C	$\delta(P_A)^a$	$\delta(P_B)^b$	$^1J(Rh-P_A)$/Hz	$^1J(Rh-P_B)$/Hz	$^1J(P_A-P_B)$/Hz	Ref.
$[RhCl(PPh_3)_3]$	CH_2Cl_2	28	48.0	31.5	189	142	38	4
	$CDCl_3$	28	48.5	31.8	191	144	39	This work
$[Rh(ONO_2)(PPh_3)_3]$	CH_2Cl_2	−30	53.8	33.2	187	148	40	This work
trans-$[Rh(CO)Cl(PPh_3)_2]$	$CHCl_3$	28	—	29.1		124	—	7
	$CDCl_3$	−30	—	28.9		126	—	This work
trans-$[Rh(CO)(ONO_2)(PPh_3)_2]$	$CDCl_3$	−30	—	31.2		131	—	This work
trans-$[Rh(CO)F(PPh_3)_2]$	CD_2Cl_2	−30	—	26.2^c		136	—	This work

[a] P_A is *trans* to X (X = Cl, ONO_2 or F). [b] P_B is due to the *trans*-$Rh(PPh_3)_2$ group. [c] $^2J(F-P_B)$ = 21.8 Hz.

Table 2 Variable-temperature ^{13}C NMR and room-temperature IR ν(CO) data for rhodium(I) complexes

Compound	Solvent	T/°C	$\delta(CO)$	$^1J(Rh-CO)$/Hz	$^1J(P-CO)$/Hz	$\tilde{\nu}(CO)/cm^{-1}$	Ref.
trans-$[Rh(CO)Cl(PPh_3)_2]$	$CDCl_3$	25	187.4	73	16	1980^a	8
	$CDCl_3$	−30	187.8	74.3	16.0	1979.5^b	This work
trans-$[Rh(CO)(ONO_2)(PPh_3)_2]$	$CDCl_3$	−30	190.9	74.7	16.9	1982^b	This work
						1971^a	7
trans-$[Rh(CO)F(PPh_3)_2]$	$CD_2Cl_2{}^c$	−30	190.6	68.8	16.8		This work

[a] In $CHCl_3$ solution. [b] In thf solution. [c] At 25 °C: $\delta(^{19}F)$ 269, $^1J(Rh-F)$ 53.6, $^2J(P-F)$ 22.6 and $^2J(CO-F)$ 77.2 Hz.

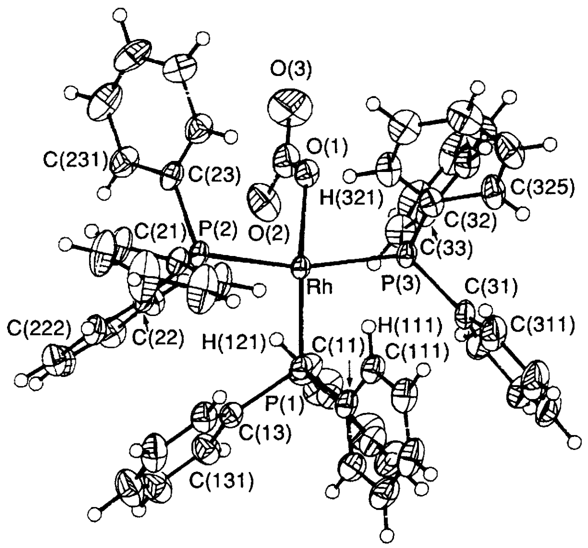


Fig. 1 Molecular structure of $[Rh(ONO_2)(PPh_3)_3]$ **2**

Table 3 Selected bond lengths (Å) and angles (°) for $[Rh(ONO_2)(PPh_3)_3]$ **2**

Rh–O(1)	2.142(4)	Rh–P(1)	2.212(3)
Rh–P(2)	2.307(3)	Rh–P(3)	2.351(3)
N–O(1)	1.294(4)	N–O(2)	1.233(4)
N–O(3)	1.222(4)	P(1)–C(11)	1.838(5)
P(1)–C(12)	1.846(5)	P(1)–C(13)	1.851(4)
P(2)–C(21)	1.830(5)	P(2)–C(22)	1.830(4)
P(2)–C(23)	1.835(5)	P(3)–C(31)	1.838(5)
P(3)–C(32)	1.837(4)	P(3)–C(33)	1.840(5)
P(1)–Rh–O(1)	169.10(5)	P(2)–Rh–O(1)	89.50(5)
P(3)–Rh–O(1)	79.00(5)	P(1)–Rh–P(2)	96.60(5)
P(1)–Rh–P(3)	97.00(5)	P(2)–Rh–P(3)	162.60(5)
Rh–O(1)–N	115.2(2)	O(1)–N–O(2)	119.2(3)
O(1)–N–O(3)	117.4(3)	O(2)–N–O(3)	123.4(4)
Rh–P(1)–C(11)	120.1(2)	Rh–P(1)–C(12)	105.5(2)
Rh–P(1)–C(13)	124.5(2)	C(11)–P(1)–C(12)	107.1(2)
C(11)–P(1)–C(13)	96.6(2)	C(12)–P(1)–C(13)	100.7(2)
Rh–P(2)–C(21)	116.5(2)	Rh–P(2)–C(22)	117.0(2)
Rh–P(2)–C(23)	113.8(2)	C(21)–P(1)–C(22)	106.0(2)
C(21)–P(2)–C(23)	99.2(2)	C(22)–P(2)–C(23)	102.0(2)
Rh–P(3)–C(31)	126.5(2)	Rh–P(3)–C(32)	109.3(2)
Rh–P(3)–C(33)	110.3(2)	C(31)–P(3)–C(32)	103.4(2)
C(31)–P(3)–C(33)	101.4(2)	C(32)–P(3)–C(33)	103.4(2)

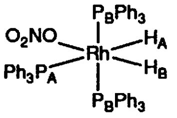
scopic evidence for this in solution. The mono-co-ordination of the NO_3 group also strongly disturbs the trigonal symmetry of the N–O bonding, with the N–ORh bond being some 0.06 Å longer than the other two N–O bonds.

A number of phenyl hydrogens also make close approaches to the metal, but again it is difficult to correlate these contacts with any form of weak association. The values for Rh–P–C angles are not helpful since those relevant to rings which contain a contacting hydrogen vary from 105° [Rh–P(1)–C(12)–Rh $\cdots$ H(121) 2.96 Å] to 120° [Rh–P(1)–C(11)–Rh $\cdots$ H(111) 3.17 Å]. The shortest contact, Rh $\cdots$ H(321) 2.84 Å, is associated with Rh–P(3)–C(32) 109°. In fact the Rh–P–C and C–P–C angles vary considerably (see Table 3) and this almost certainly results from steric crowding and ring–ring repulsions.

The $^{31}P-\{^1H\}$ NMR spectrum of compound **2** in $CDCl_3$ at low temperature is entirely in accord with the above structure (Table 1). Unfortunately, **2** is also unstable at room temperature in chlorinated solvents and insolubility precluded the use of other solvents. As a result, it was not possible to obtain NMR spectra of **2** *at room temperature* in order to gain information about phosphine lability. However, bubbling CO through a suspension of **2** in MeOH rapidly produced *trans*-$[Rh(CO)(ONO_2)(PPh_3)_2]$ which suggests that the lability of PPh_3 *trans* to ONO_2 is similar to when *trans* to Cl.[4]

Spectroscopic data on the yellow-green precipitate resulting from the above reaction in MeOH suggest it to be a mixture of two compounds, which proved impossible to separate. The ^{31}P NMR spectrum of this precipitate in $CDCl_3$ at −23 °C consists of two approximately equally intense doublets [$\delta(P)$ 30.1 and 26.8, $^1J(Rh-P)$ 103 and 84 Hz respectively] and the ^1H NMR spectrum shows a high-field doublet of triplets which we assign to coupling to rhodium and to two equivalent PPh_3 respectively [$\delta(H)$ −22.7, $^1J(Rh-H)$ 28.4, $^2J(P-H)$ 9.8 Hz]. Both values of $^1J(Rh-P)$ are significantly less than those reported in Table 1 for the rhodium(I) complexes and can thus be reasonably ascribed to phosphorus coupling to rhodium(III).

The formulations of the two compounds in this mixture, which are consistent with the spectroscopic data, are **4** and **5**. Analogous compounds containing Cl instead of ONO_2 have been described earlier.[2] Unfortunately, the mixture is only slightly soluble in most common solvents, and crystals of compounds **4** and **5** could not be obtained for X-ray analysis.



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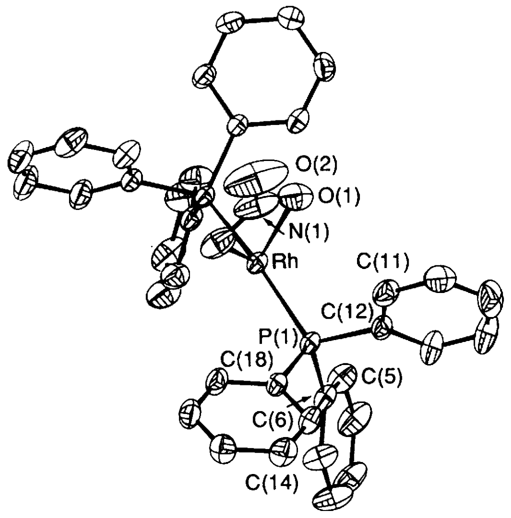
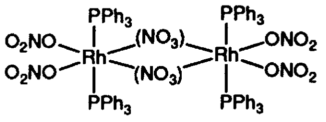


Fig. 2 Molecular structure of $[RhH_2(O_2NO)(PPh_3)_2]$ **6a**

Table 4 Selected bond lengths (Å) and angles (°) for $[RhH_2(O_2NO)(PPh_3)_2]$ **6a**

P(1)–Rh	2.301(3)	O(1)–Rh	2.252(5)
Rh–O(1a)	2.252(5)	N–O(1a)	1.269(8)
N–O(1)	1.269(5)	N–O(2)	1.249(8)
P(1)–C(6)	1.832(4)	P(1)–C(12)	1.830(4)
P(1)–C(18)	1.824(4)		
O(1)–Rh–P(1)	98.10(2)	O(1)–Rh–O(1a)	57.38(3)
P(1)–Rh–P(1a)	164.70(3)	O(1)–N–O(1a)	116.8(6)
O(1)–Rh–P(1a)	95.32(4)	O(1)–N–O(2)	121.6(3)
Rh–P(1)–C(6)	114.5(2)	Rh–P(1)–C(12)	115.8(2)
Rh–P(1)–C(18)	115.0(2)	C(6)–P(1)–C(12)	103.0(2)
C(6)–P(1)–C(18)	104.2(2)	C(12)–P(1)–C(18)	102.7(2)

Key to symmetry operations relating designated atoms to reference atoms at *x,y,z*: (a) −*x*, 1.0 − *y*, −*z*.



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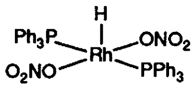

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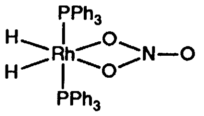
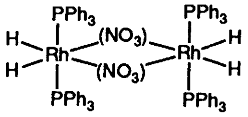


6a



6b

The reaction of $Rh(NO_3)_3{\cdot}2H_2O$ with excess of PPh_3 in acetone gives a yellow precipitate. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows one doublet [δ(P) 26.9, ^1J(Rh–P) 83.9 Hz], identical to one of the doublets described above, and there is no high-field ^1H NMR resonance. As a result, we feel this compound is identical to **4** but again X-ray-quality crystals could not be obtained.

The reaction of a suspension of compound **2** in MeOH with H_2 (1 atm) at room temperature rapidly gives $[RhH_2(ONO_2)(PPh_3)_3]$ **3**. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra in $CDCl_3$ at −23 °C and the ^{103}Rh spectrum obtained by using the insensitive nuclei enhanced by polarisation transfer (INEPT) technique on a CD_2Cl_2 solution at −60 °C respectively[*] clearly establish the stereochemistry shown, which is identical to that found for $[RhH_2Cl(PPh_3)_3]$.[4]

Unlike $[RhH_2Cl(PPh_3)_3]$, compound **3** on standing in solution loses PPh_3 to form a new hydride-containing species **6**. However, **6** is better obtained in good yield by stirring a suspension of powdered **2** in diethyl ether under an atmosphere of H_2 for 3–4 h at room temperature, whereupon it precipitates as a white solid. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows one doublet [δ(P) 39.2, ^1J(Rh–P) 119.2 Hz] and the ^1H NMR shows a high-field doublet of triplets [δ(H) −21.5, ^1J(Rh–H) 24.8, ^1J(P–H) 16.1 Hz]. Addition of PPh_3 to the solution immediately converts **6** into **3**.

INEPT measurements have been used to obtain ^{103}Rh NMR data for compound **6** in tetrahydrofuran (thf) at −60 °C. For the refocused and proton-decoupled spectrum, there is a triplet, δ(Rh) 529.4, ^1J(P–Rh) 118.1 Hz, indicating two equivalent phosphines are attached to the same rhodium atom. In the proton-coupled $^{103}Rh\text{–}^1H$ INEPT spectrum the splitting of the anti-phase pseudo-doublet, 48.7 Hz, due to rhodium–proton coupling is twice the value of ^1J(Rh–H), 24.8 Hz, obtained from ^1H NMR spectrum, which indicates that there are two equivalent protons per rhodium atom. As a result, the possible structures are **6a** and **6b**. Although a solution of **6** readily loses hydrogen under a nitrogen atmosphere, we were eventually successful in growing X-ray-quality crystals by slow diffusion of Pr^iOH into a thf solution of **6** under an atmosphere of hydrogen. The crystal structure shows the formulation to be **6a**. A diagram of the molecule is given in Fig. 2 and selected bond lengths and angles in Table 4.

The molecule lies on a two-fold axis which bisects the bidentate, chelating O_2NO group. Whilst this model corresponds to symmetrical bonding of this ligand, rather high values of some U_{ij} coefficients for component atoms suggest possible minor disorder, across the two-fold axis, of an asymmetrically bonding group. The relatively long Rh–O distance of 2.252(5) Å may also be a reflection of this situation.

Although the metal-bonded hydrogens could not be located in a difference map (in contrast to the organic hydrogens and thus perhaps indicative of acidic character of the metal hydrogens) the disposition of the remaining co-ordinated atoms is consistent with a *cis*-octahedral dihydride. The dihedral angle between the RhO_2NO and PRhP planes is 91.6(1)°. The mutually *trans* Rh–P bond lengths of 2.301(3) Å are very similar to those for the *trans* phosphines in the Rh(I) complex **2**. The reduced P–Rh–P′ angle of 164.7(3)° arises from a movement of the phosphines away from the nitrate, towards the hydride.

On losing H_2, compound **6** gives a new species **7**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum consists of one doublet [δ(P) 56.1, ^1J(Rh–P) 203.7 Hz] and the ^1H NMR spectrum does not show any high-field resonances. Addition of PPh_3 to a solution of **6** immediately gives $[Rh(ONO_2)(PPh_3)_3]$ **2**. Compound **7** can also be prepared by refluxing a benzene solution of **2** for 0.5 h followed by concentration whereupon it is obtained as a red microcrystalline precipitate. However, the yield is not high, and several other species are present in solution. Compound **7** reacts with hydrogen at room temperature and 1 atm pressure to give **6**. Hence, **7** contains rhodium(I) through

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[*] NMR data for $[RhH_2(ONO_2)(PPh_3)_3]$ **3**: in $CDCl_3$ at −23 °C, δ(P_A) 20.7, δ(P_B) 35.7, δ(H_B) −20.8, δ(H_A) −9.4, ^1J(Rh–P_A) 89.1, ^1J(Rh–P_B) 117.4, ^1J(Rh–H_B) 8.1, ^1J(Rh–H_A) 6.3, ^2J(P_A–P_B) 18.3, ^2J(P_A–H_B) 18.3, ^2J(P_A–H_A) 159.0 and ^2J(H_A–H_B) 10.6 Hz; in CD_2Cl_2 at −60 °C; δ(Rh) 270.0.

Table 5 Fractional atomic coordinates (× 10^4) for $[Rh(ONO_2)(PPh_3)_3]$ **2**

Atom	*x*	*y*	*z*
Rh	2696	2400	2255
O(1)	3406(2)	975(1)	1510(1)
O(2)	1353(2)	777(2)	1799(1)
N	2517(2)	431(2)	1452(1)
O(3)	2889(3)	−409(2)	1051(2)
P(1)	1770(1)	3655(1)	3166
C(111)	4177(3)	4155(2)	3281(1)
C(112)	4984(3)	4682(2)	3580(2)
C(113)	4449(3)	5366(2)	4198(2)
C(114)	3103(3)	5541(3)	4512(2)
C(115)	2291(3)	5031(2)	4214(2)
C(11)	2830(2)	4310(2)	3598(1)
C(121)	86(3)	2251(3)	3673(2)
C(122)	−660(3)	1653(3)	4175(2)
C(123)	−642(4)	1690(3)	4918(2)
C(124)	97(4)	2323(3)	5155(2)
C(125)	840(3)	2936(3)	4654(2)
C(12)	838(2)	2909(2)	3905(1)
C(131)	−881(3)	5103(3)	3419(2)
C(132)	−1791(3)	6126(3)	3379(2)
C(133)	−1388(4)	7023(3)	3010(2)
C(134)	−56(3)	6903(2)	2676(2)
C(135)	861(3)	5885(2)	2724(2)
C(13)	467(2)	4966(2)	3099(1)
P(2)	1780(1)	3464(1)	1342
C(211)	3463(3)	4945(3)	1291(2)
C(212)	3986(3)	5859(3)	1022(2)
C(213)	3574(4)	6466(3)	433(2)
C(214)	2692(3)	6135(3)	88(2)
C(215)	2171(3)	5229(2)	352(2)
C(21)	2519(2)	4637(2)	972(1)
C(221)	−693(3)	5140(2)	1403(1)
C(222)	−2082(3)	5470(3)	1549(2)
C(223)	−2832(3)	4718(3)	1843(2)
C(224)	−2201(3)	3631(2)	2004(2)
C(225)	−816(2)	3291(2)	1857(1)
C(22)	−39(2)	4046(2)	1549(1)
C(231)	994(3)	2531(2)	166(2)
C(232)	1273(4)	1952(3)	−503(2)
C(233)	2572(4)	1513(3)	−860(2)
C(234)	3622(3)	1643(3)	−560(2)
C(235)	3346(3)	2223(3)	105(2)
C(23)	2034(2)	2676(2)	475(1)
P(3)	4194(1)	1174(1)	2884
C(311)	3498(3)	948(3)	4425(2)
C(312)	3555(4)	1120(3)	5160(2)
C(313)	4470(5)	1651(3)	5316(2)
C(314)	5330(4)	2026(3)	4751(2)
C(315)	5272(3)	1878(2)	4019(2)
C(31)	4351(3)	1330(2)	3847(1)
C(321)	6114(3)	1397(2)	1623(2)
C(322)	7394(3)	1234(3)	1179(2)
C(323)	8497(3)	716(3)	1462(2)
C(324)	8334(3)	348(3)	2179(2)
C(325)	7061(3)	482(2)	2623(2)
C(32)	5918(2)	1017(2)	2349(1)
C(331)	4984(3)	−1228(2)	2714(2)
C(332)	4735(4)	−2293(2)	2741(2)
C(333)	3444(4)	−2415(3)	2938(2)
C(334)	2398(4)	−1474(3)	3109(2)
C(335)	2642(3)	−404(3)	3082(2)
C(33)	3946(2)	−269(2)	2891(1)

Table 6 Fractional atomic coordinates (× 10^4) for $[RhH_2(O_2NO)(PPh_3)_2]$ **6a**

Atom	*x*	*y*	*z*
Rh	0	1114(2)	2500
P(1)	−1351(1)	949(1)	2933(1)
O(1)	421(2)	2179(2)	3289(3)
O(2)	0	3210(3)	2500
N	0	2537(3)	2500
C(1)	−2558(1)	−240(1)	2680(2)
C(2)	−2770(1)	−959(1)	2809(2)
C(3)	−2073(1)	−1432(1)	3326(2)
C(4)	−1164(1)	−1187(1)	3713(2)
C(5)	−952(1)	−468(1)	3583(2)
C(6)	−1649(1)	5(1)	3066(2)
C(7)	−1444(2)	928(1)	4968(2)
C(8)	−1436(2)	1255(1)	5889(2)
C(9)	−1362(2)	2003(1)	5988(2)
C(10)	−1298(2)	2423(1)	5166(2)
C(11)	−1306(2)	2096(1)	4245(2)
C(12)	−1380(2)	1348(1)	4146(2)
C(13)	−3168(1)	1501(1)	2328(1)
C(14)	−3954(1)	1773(1)	1613(1)
C(15)	−3959(1)	1869(1)	600(1)
C(16)	−3177(1)	1692(1)	302(1)
C(17)	−2390(1)	1420(1)	1017(1)
C(18)	−2385(1)	1324(1)	2029(1)
C(20)	290(9)	4804(6)	530(10)
C(21)	734(14)	4304(13)	344(16)
C(22)	823(16)	4770(14)	4(19)
C(23)	−67(12)	4835(9)	985(14)
C(24)	894(16)	4428(12)	−915(18)

loss of H_2 from **6a** and the structure is probably $[Rh(O_2NO)(PPh_3)_2]$.

Experimental

The preparations of $[RhCl(PPh_3)_3]$ and *trans*-$[Rh(CO)Cl(PPh_3)_2]$ were carried out as described previously.[1] All solvents including deuteriated solvents, were freshly distilled and dried before use. [^{13}C]Carbon monoxide was purchased from Amersham International and ^{13}CO enrichments were carried out using standard vacuum-line procedures. Proton, ^{13}C and ^{31}P NMR spectra were obtained on a Bruker WM 200 spectrometer; ^1H and ^{13}C chemical shifts are referenced to $SiMe_4$, ^{31}P to 80% H_3PO_4 in D_2O, ^{103}Rh to 6.32 MHz at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 200 MHz; all chemical shifts are positive to high frequency of the standard. Infrared spectra were obtained as solutions using CaF_2 cells on a Perkin-Elmer 1720X FT IR spectrometer. All manipulations were carried out under an atmosphere of nitrogen.

Syntheses.—*trans*-$[Rh(CO)(ONO_2)(PPh_3)_2]$ **1**. (*i*) A solution of $Rh(NO_3)_3\cdot 2H_2O$ (1.92 g) and PPh_3 (9.71 g) in EtOH (≈500 cm^3) was refluxed for 48 h. On cooling, yellow crystals of the product **1** were obtained.

(*ii*) Bubbling CO through a suspension of $[Rh(ONO_2)(PPh_3)_3]$ in MeOH for 1 h also produced *trans*-$[Rh(CO)(ONO_2)(PPh_3)_2]$. In this case, simply concentrating the solution produced the product in near-quantitative yield.

$[Rh(ONO_2)(PPh_3)_3]$ **2**. To a solution of $Rh(NO_3)_3\cdot 2H_2O$ (0.094 g) in dry MeOH (5 cm^3) at room temperature was added a solution containing PPh_3 (1.137 g) in dry MeOH (40 cm^3). After 12 h a small amount of yellow-green precipitate had formed; this was filtered off and the resulting red solution on standing for 3–5 d deposited red crystals of compound **2**. Yield 0.165 g, 60% (Found: C, 67.95; H, 4.75; N, 1.45. Calc. for $C_{54}H_{45}NO_3P_3Rh$: C, 68.15; H, 4.75; N, 1.45%).

$[RhH_2(ONO_2)(PPh_3)_3]$ **3**. To a suspension of $[Rh(ONO_2)(PPh_3)_3]$ (0.1 g) in methanol (10 cm^3) under vacuum was added an atmosphere of H_2. The red solid started to become white and, after stirring for 30 min under the hydrogen atmosphere, the methanol was removed under vacuum and the resulting yellow-brown solid dissolved in CD_2Cl_2 under a nitrogen atmosphere.

This solution was transferred to a NMR tube under a nitrogen atmosphere for NMR measurements.

$[RhH_2(O_2NO)(PPh_3)_2]$ **6a**. Powdered $[Rh(ONO_2)(PPh_3)_3]$ (0.25 g) was suspended in dry diethyl ether (30 cm^3). The solution was put under an atmosphere of H_2 and stirred for 6 h when a white precipitate was obtained. The precipitate was filtered off, washed with ether, dried and shown to be pure by ^{31}P NMR spectroscopy and to be **6a** by X-ray crystallography.

X-Ray Crystallography.—Although all compounds are essentially air stable the crystals used for X-ray examination were sealed inside capillary tubes in an atmosphere of nitrogen. X-Ray diffraction data were recorded using an Enraf-Nonius CAD4 diffractometer operating in the ω–2θ scan mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), following standard procedures. The structures were solved *via* routine heavy-atom procedures and refined by full-matrix least squares. For compounds **2** and **6a** the analysis proceeded without problems; all non-hydrogen atoms were refined anisotropically, organic hydrogens isotropically. For **1**, however, disorder and pseudo-symmetry caused difficulties. During setting up and data collection it was noticed that all reflections with l odd were weak and more diffuse than the rest. Not surprisingly, the Patterson map showed that the two rhodiums in the cell were separated by the vector 0,0,0.5. Furthermore, peaks were easily identified to show that the phosphorus atoms were *trans* at each metal and the two P–Rh–P groups parallel. Subsequent attempts to develop the structure in $P\bar{1}$ did not allow distinction between models in which two centrosymmetric molecules (with, therefore, disorder of the CO and ONO_2 groups) were positioned at 0,0,0 and 0,0,0.5 or in which one unique molecule was sited near 0,0,0.25. In each case it proved impossible to disentangle the CO and ONO_2 disorder, and, of course, correlation caused instability in the refinement. An ideal 50/50 disorder of these groups, as was found for the triclinic form of the analogous chloride,[6] would not be consistent with the presence of the $l = 2n + 1$ reflections and these were not weak enough to be neglected. Accordingly, it was decided to abandon further attempts since the reliability of any results obtained would be limited. Nevertheless, for all models tried it was always possible to locate two *trans* atoms to represent the C of the CO and bonded O of the ONO_2 which completed a square-planar co-ordination. We are firmly of the belief now that the disorder involves not only mixing of the two ligands but also differing orientations of the monodentate nitrate group. Details of the three analyses, with limited data for the first, are as follows.

$[Rh(CO)(ONO_2)(PPh_3)_2]$ **1**, $C_{37}H_{30}NO_4P_2Rh$, M = 717.5, triclinic, space group $P1$ or $P\bar{1}$, a = 9.395(1), b = 10.386(2), c = 18.081(3) Å, α = 102.58(1), β = 101.14(1), γ = 89.95(1)°, U = 1687.9 $Å^3$, Z = 2, D_c = 1.41 g cm^{-3}, μ(Mo-Kα) = 6.28 cm^{-1}. Data collected for $1.5 < \theta < 25.0°$ giving 4400 unique reflections with 3080 observed $[F_o > 3.0\sigma(F_o)]$. A blocked refinement in $P1$ with phenyl-ring geometries constrained gave R = 0.06. The results are not reliable enough for full publication, but are included in the Supplementary material.

$[Rh(ONO_2)(PPh_3)_3]$ **2**, $C_{54}H_{45}NO_3P_3Rh$, M = 951.72, triclinic, space group $P\bar{1}$, a = 10.506(1), b = 12.187(2), c = 18.420(2) Å, α = 87.56(2), β = 77.75(2), γ = 75.81(2)°, U = 2234.3 $Å^3$, Z = 2, D_c = 1.414 g cm^{-3}, μ(Mo-Kα) = 5.20 cm^{-1}. Data were collected for $1.5 < \theta < 25.0°$ giving 7864 unique reflections and 6702 observed $[F_o > 3\sigma(F_o)]$. Full-matrix refinement with 739 parameters gave R, R' values of 0.0246, 0.0247 respectively with $w = [\sigma^2(F_o) + 0.002\ F_o^2]$. Final coordinates are given in Table 5.

$[RhH_2(O_2NO)(PPh_3)_2]$ **6a**, $C_{36}H_{30}NO_3P_2Rh$·solvent, M = 751.71 (with solvent $\equiv C_5$), monoclinic, space group $C2/c$, a = 15.085(2), b = 18.561(5), c = 13.681(2) Å, β = 106.89(4)°, U = 3665.4 $Å^3$, Z = 4, D_c = 1.36 g cm^{-3}, μ(Mo-Kα) = 5.80 cm^{-1}. Data were collected for $1.5 < \theta < 25.0°$, giving 3226 unique reflections and 2909 observed $[F_o > 3\sigma(F_o)]$. Full-matrix refinement with 183 parameters (phenyl rings treated as rigid hexagons, ring hydrogens in idealised positions with group U_{iso} values, all non-hydrogens anisotropic) gave R = 0.044, R' = 0.063, with $w = [\sigma^2(F_o) + 0.007F_o^2]^{-1}$. Final coordinates are given in Table 6. Some disordered solvent of crystallisation present was represented by five carbon atoms. These did not represent any recognisable molecule.

Computer programs used SHELX 76[9] and SNOOPI.[10]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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