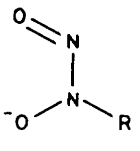
Metal Complexes of *N*-Aryl-*N*-nitrosohydroxylamines: Cleavage of N–N Bonds to give Metal Nitrosyl Species and Organonitrogen Compounds, and the Crystal Structure of $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]\cdot 0.5Me_2CO$[†]

Mushtaq Ahmed, Anthony J. Edwards,* Christopher J. Jones, Jon A. McCleverty,* Anne S. Rothin, and John P. Tate
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Reaction of $[RhCl(PPh_3)_3]$, $[Rh_2(CO)_4Cl_2]$, $[Rh_2(\eta\text{-}C_5Me_5)_2Cl_4]$, $[RuCl_2(PPh_3)_3]$, and $[Pd(Ph)Cl(PPh_3)_2]$ with $Q[ONN(R)O]$ ($Q = NH_4$ or Ag; R = Ph or $C_6H_4Me\text{-}p$) afforded $[RhL_2\{ONN(R)O\}]$ ($L = PPh_3$ or CO), $[Rh(\eta\text{-}C_5Me_5)Cl\{ONN(R)O\}]$, $[Ru\{ONN(R)O\}_2(PPh_3)_2]$, and $[PdPh\{ONN(R)O\}(PPh_3)]$. Reaction of $[Rh\{ONN(R)O\}(PPh_3)_2]$ with I_2 gave $[\{RhI_x[ONN(R)O](PPh_3)_2\}_n]$ (R = Ph, $x = 2$, $n = 1$; R = $C_6H_4Me\text{-}p$, $x = 1$, n = unknown), and with CO gave $[Rh(CO)\{ONN(R)O\}(PPh_3)]$. The latter was also prepared from $[Rh(CO)_2\{ONN(R)O\}]$ and PPh_3. Treatment of $[Rh\{ONN(R)O\}(PPh_3)_2]$ and $[Ru\{ONN(R)O\}_2(PPh_3)_2]$ with $RhCl_3$ and $RuCl_3$ afforded $[RhCl_2\{ONN(R)O\}(H_2O)(PPh_3)]$ and $[RuCl\{ONN(R)O\}_2(PPh_3)_2]$, respectively. The structure of $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]\cdot 0.5Me_2CO$ was determined crystallographically, and the metal shown to be six-co-ordinate with a chelating *N*-aryl-*N*-nitrosohydroxylaminato ligand and water. Treatment of $[PdPh\{ONN(R)O\}(PPh_3)]$, $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$, and $[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$ with HCl gave $[Pd_2Cl_4(PPh_3)_2]$, $[RhCl_2(NO)(PPh_3)_2]$, and $[RuCl_3(NO)(PPh_3)_2]$, respectively, and the organic products obtained from the complexes of Rh and Ru identified by gas chromatography and mass spectrometry as $p\text{-}MeC_6H_4NO$, $p\text{-}MeC_6H_4NH_2$ (major component), and $C_6H_3Me(NH_2)Cl$. A possible mechanism of formation of the nitrosyl complexes and organonitrogen compounds is briefly discussed.

The insertion of NO into metal–carbon bonds of d^0 and d^{10} transition-metal alkyls affords compounds containing *N*-alkyl-*N*-nitrosohydroxylamido ligands, (**1**).[1] For example, treatment of $[WMe_6]$ and $[ZnMe_2]$ with NO gave $[WMe_4\{ONN(Me)O\}_2]$, whose structure was confirmed crystallographically,[2] and $[Zn\{ONN(Me)O\}_2]$, which reacted with aqueous Cu^{2+} giving $[Cu\{ONN(Me)O\}_2]$.[3]



(**1**)

A potential catalytic cycle for the formation of organonitrogen compounds involving the use of NO with metal alkylating agents might involve the intermediacy of species containing (**1**). Consequently, a knowledge of the stability of metal complexes of these ligands, particularly towards N–N bond cleavage and formation of metal-free organonitrogen fragments, would be useful.

Complexes of *N*-nitroso-*N*-phenylhydroxylamine[‡] have been prepared, and the structures of such species as $[Fe\{ONN(Ph)O\}_3]$[4] and $[Cu\{ONN(Ph)O\}_2]$[5] determined crystallographically. The 'Cupferron ion,' $[ONN(Ph)O]^-$, and its *p*-tolyl analogue, $[ONN(C_6H_4Me\text{-}p)O]^-$, are readily prepared, and, as a result of a chance observation that reactions of $[NH_4][ONN(Ph)O]$ with certain rhodium(I) complexes on occasion afforded rhodium nitrosyl species, we have systematically examined the properties of several different metal complexes of ligands of type (**1**), where R = aryl. Related complexes of (**1**; R = Me) have also been described, and although these were obtained by reaction of NO with transition-metal methyl complexes, their decomposition to organonitrogen complexes was not explored.[6]

Experimental

Cupferron, $[NH_4][ONN(Ph)O]$, and its *p*-tolyl and 2-naphthyl analogues, $[NH_4][ONN(C_6H_4Me\text{-}p)O]$ and $[NH_4][ONN(C_{10}H_7)O]$, were prepared by methods described in the literature.[7]

Elemental analyses were carried out by the Microanalytical Laboratories of the Universities of Sheffield and Birmingham. I.r. spectra were obtained using a PE 297 spectrophotometer, and ^1H n.m.r. spectra using OE R34 and Varian HA100 instruments. Mass spectra were recorded using AEI-MS12 and Kratos MS-80 instruments, the latter fitted with a Carlo Erba 4200 gas chromatograph. Gas chromatographic work was carried out using a Pye 104 instrument with flame ionization detection and an OV-17 column (3% on Ultrasorb) at 125 °C. All melting points were uncorrected, and yields are quoted relative to the starting material. All reactions were carried out under nitrogen.

$Ag[ONN(Ph)O]$.—To a solution of $AgNO_3$ (0.5 g, 2.9 mmol) in water (5 cm^3) was added a solution of $[NH_4][ONN(Ph)O]$ (0.46 g, 3 mmol) in ethanol (20 cm^3). The mixture was stirred vigorously in the absence of light for 15 min, and the suspension treated with n-hexane to complete precipitation of the salt. The white solid so formed was filtered off, washed with diethyl ether

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[†] Aquadichloro(*N*-nitroso-*N*-*p*-tolylhydroxylamido-*OO′*)(triphenylphosphine)rhodium–acetone (2/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

[‡] $[NH_4][ONN(Ph)O]$ is known as Cupferron, a well established analytical agent for Fe and Cu.

and n-hexane, and dried *in vacuo* {0.53 g, 74% based on $[NH_4][ONN(Ph)O]$}. The salt $Ag[ONN(C_6H_4Me\text{-}p)O]$ was prepared similarly, and both compounds were stored in the dark and used as soon as possible after their precipitation.

$[Rh\{ONN(Ph)O\}(PPh_3)_2]$.—The compounds $[RhCl(PPh_3)_3]$ (0.46 g, 0.5 mmol) and $[NH_4][ONN(Ph)O]$ (0.08 g, 0.5 mmol) were heated in degassed anhydrous ethanol (30 cm^3) at 40—45 °C for 3 h, and the mixture then cooled to room temperature. The orange solid was filtered off, washed with a small amount of ethanol, and dried *in vacuo* (yield 1.52 g, 90%). The related complexes $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ and $[Rh\{ONN(C_{10}H_7)O\}(PPh_3)_2]$ were obtained similarly, as orange solids.

$[Rh(CO)_2\{ONN(Ph)O\}]$.—The compounds $[Rh_2(CO)_4Cl_2]$ (0.19 g, 0.7 mmol) and $[NH_4][ONN(Ph)O]$ (0.16 g, 1.0 mmol) in anhydrous ethanol (30 cm^3) were stirred at room temperature for 15—20 min, during which time a yellow solid precipitated. This was collected by filtration and recrystallised from ethanol, affording the complex as yellow crystals (yields variable). The compound $[Rh(CO)_2\{ONN(C_6H_4Me\text{-}p)O\}]$ was prepared similarly as yellow crystals.

$[Rh(CO)\{ONN(Ph)O\}(PPh_3)]$.—A suspension of $[Rh(CO)_2\{ONN(Ph)O\}]$ (0.1 g, 0.3 mmol) and PPh_3 (0.09 g, 0.3 mmol) in anhydrous ethanol (30 cm^3) was stirred at room temperature for 15 min. The yellow precipitate which formed was filtered off and dried in air (yield 0.12 g, 68%).

$[Rh(CO)\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)]$.—*Method 1.* This complex was prepared in the same way as its phenyl analogue above (yields 60%).

Method 2. Carbon monoxide was bubbled through a stirred solution of $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ (0.14 g) in refluxing toluene (30 cm^3) for 5 h. The dark red solution was then evaporated *in vacuo* to *ca.* 10 cm^3 and kept at 0 °C for 1 week. The solid which had formed was filtered off and recrystallised from dichloromethane–n-hexane mixtures. The complex was obtained as greenish yellow crystals (0.07 g, 66%).

$[RhI_2\{ONN(Ph)O\}(PPh_3)_2]$.—A suspension of $[Rh\{ONN(Ph)O\}(PPh_3)_2]$ (0.2 g, 0.25 mmol) and iodine (0.06 g, 0.1 mmol) in light petroleum (b.p. 80—100 °C; 25 cm^3) was stirred for 18 h. The brown precipitate was then filtered off and recrystallised from dichloromethane–n-hexane mixtures, affording the complex as brown crystals (0.19 g, 75%).

$[\{RhI\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2\}_n]$.—This compound was prepared in the same way as the phenyl compound above, using $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ (0.26 g, 0.3 mmol) and iodine (0.04 g, 0.16 mmol), and was obtained as brown crystals (yield 0.2 g, 66%).

$[RhCl_2\{ONN(Ph)O\}(H_2O)(PPh_3)]$.—A mixture of $[Rh\{ONN(Ph)O\}(PPh_3)_2]$ (0.19 g, 0.2 mmol) and $RhCl_3\cdot3H_2O$ (0.07 g, 0.2 mmol) in ethanol (30 cm^3) was stirred at room temperature for 18 h. The brown solid which had formed was filtered off, dissolved in acetone, and chromatographed on silica gel (acetone–n-hexane mixtures as eluant). The brown fraction was collected, the solvent evaporated *in vacuo*, and the residue recrystallised from acetone–n-hexane mixtures affording the complex as a brown solid (yield 0.1 g, 68%). The compound $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]\cdot0.5Me_2CO$ was obtained similarly using $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ (0.19 g, 0.2 mmol) and $RhCl_3\cdot3H_2O$ (0.07 g, 0.2 mmol) and isolated as brown crystals (yield 0.1 g, 60%).

$[Rh(\eta\text{-}C_5Me_5)Cl\{ONN(Ph)O\}]$.—The compounds $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.15 g, 0.03 mmol) and $[NH_4][ONN(Ph)O]$ (0.15 g, 1.0 mmol) in ethanol (30 cm^3) were stirred together at 40—45 °C for 3 h. The solid which had precipitated was then filtered off, washed with ethanol, and dried *in vacuo*, affording the complex as an orange powder (yield quantitative). The compound $[Rh(\eta\text{-}C_5Me_5)Cl\{ONN(C_6H_4Me\text{-}p)O\}]$ was prepared similarly.

$[Ru\{ONN(Ph)O\}_2(PPh_3)_2]$.—The compounds $[RuCl_2(PPh_3)_2]$ (0.32 g, 0.5 mmol) and $[NH_4][ONN(Ph)O]$ (0.21 g, 1.4 mmol) in methanol (30 cm^3) were stirred at 40—45 °C for 3 h. The mixture was then cooled to room temperature, and the red-brown complex filtered off and dried *in vacuo* (yields 40—50%). The compound $[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$ was prepared similarly using $[RuCl_2(PPh_3)_3]$ (2.0 g) and $[NH_4][ONN(C_6H_4Me\text{-}p)O]$ (1.14 g), as a red-brown solid (yield 0.85 g, 44%).

$[RuCl\{ONN(Ph)O\}_2(PPh_3)_2]$.—A mixture of $[Ru\{ONN(Ph)O\}_2(PPh_3)_2]$ (0.11 g, 0.1 mmol) and $RuCl_3\cdot3H_2O$ (0.03 g, 0.1 mmol) in methanol (30 cm^3) was stirred and refluxed at 70 °C for 18 h. On cooling to room temperature (r.t.), a brown solid precipitated and this was filtered off, dissolved in acetone, and chromatographed on silica gel using acetone–n-hexane mixtures as eluant. The brown fraction was collected and the solvent evaporated *in vacuo*. The residue was recrystallised from acetone–n-hexane mixtures, giving the complex as brown microcrystals (yield 0.1 g, 85%). The compound $[RuCl\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$ was prepared similarly using $[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$ (0.12 g) and $RuCl_3\cdot3H_2O$ (0.03 g), as a brown solid (yield 0.09 g, 75%).

$[PdPh\{ONN(Ph)O\}(PPh_3)_2]$.—The salt $Ag[ONN(Ph)O]$ (0.17 g, 0.7 mmol) was added to a solution of $[Pd(Ph)Cl(PPh_3)_2]$ (0.5 g, 0.7 mmol) in benzene (30 cm^3). The mixture was stirred vigorously overnight at r.t. in the absence of light. The resulting solution was filtered affording white $[\{AgCl(PPh_3)_4]$ and a pale yellow filtrate. The filtrate was reduced to low bulk *in vacuo* and treated with n-hexane. Further evaporation *in vacuo* gave a cream-yellow solid which was filtered off and recrystallised from dichloromethane–n-hexane mixtures. The solid was dried *in vacuo* affording the cream complex (yield 0.28 g, 71%). The compound $[Pd(Ph)\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)]$ was prepared similarly using $[Pd(Ph)Cl(PPh_3)_2]$ (0.5 g) and $Ag[ONN(C_6H_4Me\text{-}p)O]$ (0.18 g), and isolated as a cream solid (yield 0.3 g, 75%).

Reactions of Various Complexes containing $[ONN(C_6H_4Me\text{-}p)O]^-$ *with Concentrated* HCl.—(*a*) A suspension of $[PdPh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)]$ (0.75 g) in concentrated HCl (30 cm^3) was stirred and heated at 80—90 °C for 12 h. After cooling to r.t., the orange solid formed was filtered off and crystallised from chloroform–light petroleum (b.p. 40—60 °C) mixtures. The orange microcrystalline product, which was dried *in vacuo*, was identified as $[Pd_2Cl_4(PPh_3)_2]$ (yield 0.27 g, 49%).

(*b*) The compound $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ (0.7 g) was suspended in diethyl ether (25 cm^3) and concentrated HCl (0.16 cm^3) was added. The mixture was stirred and refluxed for 3 h, and the resulting suspension cooled to room temperature and filtered. The solid residue was washed with diethyl ether and dried *in vacuo*, affording $[RhCl_2(NO)(PPh_3)_2]$ (yield 0.61 g, 92%). The ether extracts were studied using gas chromatography and mass spectrometry (see below).

(*c*) The compound $[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$ (0.3 g) and concentrated HCl (0.12 cm^3) were refluxed together in diethyl ether (25 cm^3) for 12—15 h. The resulting suspension was cooled and filtered in air, the solid residue being washed with diethyl ether. The yellow-brown complex, obtained by recrystallisation from dichloromethane–n-hexane mixtures, was identified as $[RuCl_3(NO)(PPh_3)_2]$ (yield 0.22 g, 87%).

Gas Chromatographic–Mass Spectral (g.c.–m.s.) Studies of Ether Extracts obtained after Treatment of Complexes containing $[ONN(C_6H_4Me\text{-}p)O]^-$ *with Concentrated* HCl.—(*a*) *Products obtained from* $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$. Three g.c. peaks were detected. Peak 1 was identified as *p*-nitrosotoluene by peak matching with an authentic sample; *m*/*z* 121 (73), 91 (100), 89 (12), 65 (85), 63 (20), 51 (15), and 50 (11%); *p*-MeC_6H_4NO gives *m*/*z* = 121 (84, $[M]^+$), 91 (100, $[C_7H_7]^+$), 89 (12), 65 (70, $[C_5H_5]^+$), 63 (15), 51 (8), and 50 (7%). Peak 2 was identified in the same way as *p*-toluidine; *m*/*z* = 107 (75), 106 (100), 91 (3), 89 (2), 77 (12), 65 (3), 63 (3), and 53 (8%); *p*-$MeC_6H_4NH_2$ gives *m*/*z* = 107 (72, $[M]^+$), 106 (100, $[M - H]^+$), 91 (3, $[C_7H_7]^+$), 89 (2), 77 (11, $[C_6H_5]^+$), 65 (3, $[C_5H_5]^+$), 63 (2), and 53 (4%). Peak 3: *m*/*z* = 143 (32), 142 (35), 141 (100), 140 (79), 106 (91), 79 (10), 77 (28), and 52 (18%); 2-amino-4-chlorotoluene gives *m*/*z* = 143 (33, $[M]^+$ based on ^{37}Cl), 141 (100, $[M^+]$ based on ^{35}Cl), 140 (35, $[M - H]^+$), 106 (91, $[M - Cl]^+$), 79 (11), 77 (26), and 52 (12%).

(*b*) *Products obtained from* $[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$. Three g.c. peaks were identified. Peak 1 was identified as in (*a*) above as *p*-MeC_6H_4NO: *m*/*z* = 121 (100, $[M]^+$), 91 (83, $[C_7H_7]^+$), 89 (8), 77 (2), 65 (30, $[C_5H_5]^+$), 51 (3), and 50 (3%). Peak 2 was identified as in (*a*) above as *p*-$MeC_6H_4NH_2$: *m*/*z* = 107 (65, $[M]^+$), 106 (100, $[M - H]^+$), 91 (2, $[C_7H_7]^+$), 89 (3), 77 (6, $[C_6H_5]^+$), 65 (2, $[C_5H_5]^+$), 63 (2), and 53 (3%). Peak 3 was identified as 2-amino-4-chlorotoluene: *m*/*z* = 143 (34, $[M]^+$ based on ^{37}Cl), 142 (35, $[M - H]^+$), 141 (100, $[M]^+$ based on ^{35}Cl), 140 (85, $[M - H]^+$), 106 (80, $[M - Cl]^+$), 79 (5), 71 (17), and 52 (3%).

Crystallographic Determination of $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]\cdot 0.5Me_2CO$.—Crystals were obtained from acetone–n-hexane mixtures as dark red blocks. Unit-cell and space-group data were initially investigated photographically, and intensity data and accurate cell dimensions subsequently measured with a diffractometer.

Crystal data. $C_{25}H_{24}Cl_2N_2O_3PRh\cdot 0.5(CH_3)_2CO$, *M* = 634 (excluding solvent, 605), triclinic, $a = 10.581(2)$, $b = 10.626(1)$, $c = 13.148(10)$ Å, $\alpha = 99.00(4)$, $\beta = 108.89(4)$, $\gamma = 95.24(1)°$, $U = 1\,365$ Å^3, $Z = 2$, $D_c = 1.54$ g cm^{-3}, $F(000) = 612$, space group $P\bar{1}$ (C_i^1, no. 2), Mo-K_α radiation ($\lambda = 0.7107$ Å, $\mu = 8.4$ cm^{-1}).

Intensity data. After the preliminary photographic investigations the crystal was mounted on an Enraf-Nonius CAD-4 diffractometer of the Crystallography Unit, Universities of Aston and Birmingham. Accurate cell dimensions and intensity data were obtained by the standard methods described previously.[8] Within the range $2 < 2\theta < 55°$, 4 261 independent reflections having $I > 2.5\sigma(I)$ were observed. Two standard reflections were measured every hour and showed no variation with time. Data were corrected for Lorentz and polarisation factors but not for absorption.

Structure determination. The structure was solved by conventional Patterson–Fourier techniques. The scattering factors used were those for neutral atoms.[9] Refinement by full-matrix least-squares methods was carried out initially with all atoms vibrating isotropically. Although the complete identity of the compound was not known when the analysis was started, the two chlorine atoms and the triphenylphosphine and $ONN(C_6H_4Me\text{-}p)O^-$ ligands were easily recognised, and the presence of a water molecule in the sixth octahedral co-ordination position was deduced from the size of the peak in a difference synthesis, and from the normal value for the thermal parameter on refinement of the oxygen atom position.

After the initial refinement was complete ($R = 0.086$), anisotropic thermal parameters were introduced for the rhodium, phosphorus, and chlorine atoms, and hydrogen atoms in calculated positions included in the structure-factor calculations, without refinement, and with a common, isotropic thermal parameter. A difference synthesis showed some small features near to the oxygen atom of the water molecule, but not in positions assignable to hydrogen atoms. Four larger peaks at *ca.* 2—3 e Å^{-3} also appeared around the special position ($\frac{1}{2}$, $\frac{1}{2}$, 1) and were assigned to a disordered acetone molecule. The disorder appeared not to be simple, as no geometric relationship between the peaks could be deduced. However, these four peaks, and the four peaks related by the centre of symmetry, are approximately planar, in line with the assumption of an acetone molecule. A model with the oxygen and two methyl carbon

Table 1. Final atomic positional parameters with estimated standard deviations (e.s.d.s) in parentheses for the compound $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]\cdot 0.5Me_2CO$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	0.007 81(3)	0.387 16(3)	0.170 14(3)	C(25)	0.171 4(5)	0.398 8(5)	0.575 4(5)
P	0.117 6(1)	0.240 4(1)	0.255 0(1)	C(26)	0.312 3(6)	0.416 8(5)	0.627 1(5)
Cl(1)	−0.187 7(1)	0.314 2(1)	0.200 5(1)	C(31)	0.015 8(4)	0.090 8(4)	0.252 5(4)
Cl(2)	−0.054 7(1)	0.253 9(1)	−0.002 9(1)	C(32)	0.040 6(5)	0.038 7(4)	0.347 7(4)
O(1)	−0.095 2(3)	0.536 1(3)	0.091 9(3)	C(33)	−0.026 6(5)	−0.081 0(5)	0.341 9(5)
O(2)	0.071 1(3)	0.527 6(3)	0.307 7(3)	C(34)	−0.079 6(5)	0.022 7(5)	0.153 2(4)
O(3)	0.172 7(3)	0.478 0(3)	0.151 6(2)	C(35)	−0.145 7(5)	−0.096 7(5)	0.148 6(5)
N(1)	0.178 9(4)	0.601 6(3)	0.303 8(3)	C(36)	−0.117 2(5)	−0.149 6(5)	0.242 8(4)
N(2)	0.232 5(4)	0.579 9(4)	0.230 0(3)	C(41)	0.248 7(4)	0.189 1(4)	0.202 8(4)
C(11)	0.222 9(5)	0.710 7(5)	0.493 0(4)	C(42)	0.357 1(5)	0.277 6(5)	0.207 0(4)
C(12)	0.232 9(5)	0.714 5(4)	0.390 3(4)	C(43)	0.243 6(5)	0.060 4(5)	0.157 3(4)
C(13)	0.326 0(5)	0.935 2(5)	0.552 3(4)	C(44)	0.458 9(6)	0.239 5(5)	0.170 3(5)
C(14)	0.270 6(5)	0.821 9(5)	0.574 6(5)	C(45)	0.454 1(6)	0.112 9(5)	0.126 7(5)
C(15)	0.332 3(5)	0.934 3(5)	0.448 3(4)	C(46)	0.344 4(6)	0.022 6(6)	0.118 8(5)
C(16)	0.286 9(5)	0.825 3(5)	0.365 3(4)	C(5)	0.374 0(6)	1.056 3(6)	0.642 4(5)
C(21)	0.117 5(5)	0.345 0(5)	0.462 2(4)	O(s1)*	0.3488	0.4193	0.9154
C(22)	0.201 1(4)	0.308 8(4)	0.402 1(4)	C1(s1)*	0.4310	0.5020	0.9910
C(23)	0.341 2(5)	0.326 1(5)	0.455 7(4)	C2(s1)*	0.5799	0.5036	1.0138
C(24)	0.394 0(6)	0.382 0(6)	0.569 7(5)	C3(s1)*	0.4370	0.6270	1.0662

* Included at half occupancy.

Table 2. Analytical and m.p. data for new compounds

Compound	Analysis/%						M.p./°C
	Found			Required			
	C	H	N	C	H	N	
$[\mathrm{Rh\{ONN(Ph)\}(PPh_3)_2}]$	66.1	4.8	3.8	66.0	4.6	3.7	133
$[\mathrm{Rh\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}(PPh_3)_2}]$	66.0	4.7	3.8	66.3	4.8	3.6	148
$[\mathrm{Rh\{ONN(C_{10}H_7)O\}(PPh_3)_2}]$	67.6	4.6	3.2	67.8	4.6	3.4	122
$[\mathrm{Rh(CO)_2\{ONN(Ph)O\}}]$	32.6	1.9	9.5	32.5	1.7	9.5	82
$[\mathrm{Rh(CO)_2\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}}]$	34.7	2.5	9.0	34.9	2.3	9.0	86
$[\mathrm{Rh(CO)\{ONN(Ph)O\}(PPh_3)}]$	56.3	4.2	5.3	56.6	3.8	5.3	160
$[\mathrm{Rh(CO)\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}(PPh_3)}]$	57.0	4.2	5.0	57.4	4.1	5.2	184
$[\mathrm{RhI_2\{ONN(Ph)O\}(PPh_3)_2}]$	50.5[a]	3.4	2.6	49.5[a]	3.5	2.8	158
$[\{\mathrm{RhI\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}(PPh_3)_2}\}_n]$	56.8[b]	4.2	3.0	57.0[b]	4.1	3.1	166
$[\mathrm{RhCl_2\{ONN(Ph)O\}(H_2O)(PPh_3)}]$	57.3[c]	4.3	5.0	57.4[c]	4.1	5.2	122
$[\mathrm{RhCl_2\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}(H_2O)(PPh_3)}]\cdot\mathrm{0.5Me_2CO}$	52.8[d]	4.7	4.4	50.2[d]	4.3	4.4	170
$[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl\{ONN(Ph)O\}}]$	46.9[e]	5.1	7.0	46.8[e]	4.9	6.8	190 (decomp.)
$[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}}]$	47.9[f]	5.4	6.8	48.1[f]	5.2	6.6	180 (decomp.)
$[\mathrm{Ru\{ONN(Ph)O\}_2(PPh_3)_2}]$	64.0	4.4	6.1	64.1	4.5	6.2	135
$[\mathrm{Ru\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}_2(PPh_3)_2}]$	64.5	4.5	5.8	64.7	4.8	6.0	143
$[\mathrm{RuCl\{ONN(Ph)O\}_2(PPh_3)_2}]$	62.9[g]	4.8	6.2	61.6[g]	4.3	6.0	155
$[\mathrm{RuCl\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}_2(PPh_3)_2}]$	62.3[h]	4.3	6.1	62.3[h]	4.6	5.8	146
$[\mathrm{PdPh\{ONN(Ph)O\}(PPh_3)}]$	61.6	4.5	4.5	61.8	4.3	4.8	
$[\mathrm{PdPh\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}(PPh_3)}]$	62.6	4.9	4.2	62.4	4.6	4.7	
$[\mathrm{PdCl_4(PPh_3)_2}]$	49.5	3.6		49.2	3.4		
$[\mathrm{RhCl_2(NO)(PPh_3)_2}]$	59.7	4.3	2.0	59.4	4.2	1.9	
$[\mathrm{RuCl_3(NO)(PPh_3)_2}]$	56.2	4.0	1.8	56.7	4.0	1.8	

[a] I: found 25.0, calc. 24.9%. [b] I: found 14.8, calc. 14.0%. [c] Cl: found 11.6, calc. 12.0%. [d] Cl: found 11.0, calc. 11.1%. [e] Cl: found 8.6, calc. 8.6%. [f] Cl: found 8.4, calc. 8.4%. [g] Cl: found 3.5, calc. 3.8%. [h] Cl: found 3.8, calc. 3.7%.

atoms assigned to three of these peaks and the central carbon atom in a calculated position (all at half occupancy) gave reasonable bond lengths and an acceptable geometry, while only raising R to 0.042, compared with a value of 0.041 when the four peaks were refined as carbon atoms at half occupancy. This two-fold disordered molecule thus accounts for the main features, but probably does not represent a complete description of the disorder. In the final stages weights derived from the counting statistics were found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.1\sigma$, the final R was 0.041 and $R' \{= [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}\} =$ 0.047. The calculations were carried out on an ICL 1906A computer at Birmingham University Computer Centre and on a CDC 7600 computer at the University of Manchester Regional Computer Centre using the program SHELX 76.[10] Final positional parameters with their estimated standard deviations are listed in Table 1.

Results and Discussion

Synthesis and Spectral Characterisation of Complexes containing $[\mathrm{ONN(R)O}]^-$ *(R = Ph or* $\mathrm{C_6H_4Me}$-p*).*—Treatment of $[\mathrm{RhCl(PPh_3)_3}]$, $[\mathrm{Rh_2(CO)_4Cl_2}]$, $[\mathrm{Rh_2(\eta\text{-}C_5Me_5)_2Cl_4}]$, and $[\mathrm{RuCl_2(PPh_3)_3}]$ with $[\mathrm{NH_4}][\mathrm{ONN(R)O}]$ afforded the complexes $[\mathrm{Rh\{ONN(R)O\}(PPh_3)_2}]$, $[\mathrm{Rh(CO)_2\{ONN(R)O\}}]$, $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl\{ONN(R)O\}}]$, and $[\mathrm{Ru\{ONN(R)O\}_2(PPh_3)_2}]$ (analytical and m.p. data in Table 2). The phenylpalladium(II) complexes $[\mathrm{PdPh\{ONN(R)O\}(PPh_3)}]$ were obtained from $[\mathrm{Pd(Ph)Cl(PPh_3)_2}]$ using $\mathrm{Ag}[\mathrm{ONN(R)O}]$.

The i.r. spectra of these complexes exhibited strong absorptions in the regions 1 380—1 330, 1 305—1 265, 1 215—1 170, and 940—900 cm^{-1} (for selected complexes, see Table 3). These spectra were very similar to those observed for $[\mathrm{Fe\{ONN(Ph)O\}_3}]$ and $[\mathrm{Cu\{ONN(Ph)O\}_2}]$.[11] The bands in the region 940—900 cm^{-1} may be associated with N–O or N–N stretching modes, or combinations of these, and those in the ranges 1 305—1 265 and 1 215—1 170 cm^{-1} with N=O vibrations although the NO bond order in these complexes is probably lower than 2 [ν(NO) for RNO at 1 564 (R = Me), 1 558 (R = $\mathrm{C_6H_{11}}$), and 1 488—1 513 cm^{-1} (R = aryl)]. The complexes $[\mathrm{PdPh\{ONN(R)O\}(PPh_3)}]$ also exhibited a sharp band of medium intensity at 1 565 cm^{-1}, which is characteristic of the Pd–Ph group, being probably the C–H out-of-plane bending mode.[12] Those complexes containing CO groups exhibited strong bands in the region 1 960—2 100 cm^{-1} (see Table 3).

The ^{1}H n.m.r. spectra of the new complexes containing the $[\mathrm{ONN(R)O}]^-$ ligands (R = Ph or $\mathrm{C_6H_4Me}$-p) were generally uninformative, since most of the resonances overlapped with those of $\mathrm{PPh_3}$.

Reactions of $[\mathrm{M\{ONN(R)O\}}_x\mathrm{(PPh_3)_2}]$ *(M = Rh,* $x = 1$*; M = Ru,* $x = 2$*).*—During the preparation of $[\mathrm{Rh\{ONN(R)O\}(PPh_3)_2}]$ we occasionally observed the formation of $[\mathrm{Rh(NO)(PPh_3)_3}]$ and $[\mathrm{RhCl_2(NO)(PPh_3)_2}]$. In an effort to understand these reactions, which appear to involve decoupling of the N–N bond in the $\overline{\mathrm{MONN(R)O}}$ ring, we investigated the behaviour of $[\mathrm{Rh\{ONN(R)O\}(PPh_3)_2}]$ with some nucleophiles and electrophiles which might conceivably have been present as impurities in the $[\mathrm{RhCl(PPh_3)_3}]$ used as precursor for these 'Cupferron' complexes.

There was no apparent reaction between $[\mathrm{Rh\{ONN(R)O\}(PPh_3)_2}]$ and various molar ratios of $\mathrm{PPh_3}$ (1:1, 1:2, 1:4, 1:8, or 1:16). When CO was passed into refluxing toluene solutions containing $[\mathrm{Rh\{ONN(C_6H_4Me\text{-}}p\mathrm{)O\}(PPh_3)_2}]$, the monocar-

Table 3. Infrared spectral data (cm^{-1}) obtained for selected complexes (KBr discs)

Compound	Bands characteristic of $[ONN(C_6H_4Me\text{-}p)O]^-$	Other bands
$[NH_4][ONN(C_6H_4Me\text{-}p)O]$	1 330vs, 1 278vs, 1 215vs, 918vs	3 250—2 800vs, br (NH_4^+), 1500s, 1 450—1 390s, br, 1 310s, 1 120m, 1 060s, 1 015w, 830m, 810s, 795s, 625vs
$Ag[ONN(C_6H_4Me\text{-}p)O]$	1 335s, 1 275s, 1 230s, 920s	3 050w, 2 925w, 1 500s, 1 415m, 1 310m, 1 150w, 1 120w, 1 105w, 1 062m, 835m, 815vs, 800m, 630s
$[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$	1 340s, 1 285s, 1 190s, 912s	3 075w, 3 060m, 1 590w, 1 575w, 1 502m, 1 480m, 1 438s, 1 310m, 1 175m, 1 100vs, 1 065w, 1 035w, 1 020w, 1 005w, 822s, 750s, 705s, 700s
$[Rh(CO)_2\{ONN(C_6H_4Me\text{-}p)O\}]$	1 335s, 1 285s, 1 190s, 915s	3 050w, 2 925w, 2 080s (CO), 2 040s (CO), 1 500s, 1 415m, 1 310m, 1 150w, 1 120w, 1 105w, 1 062m, 835m, 815vs, 800m, 630s
$[Rh(CO)\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)]$	1 340s, 1 275s, 1 220s, 918s	3 070w, 2 930w, 1 975s (CO), 1 590m, 1 575w, 1 500m, 1 475m, 1 440s, 1 310m, 1 180m, 1 105vs, 1 060w, 1 035w, 1 025w, 1 000w, 822s, 750s, 710s, 700s
$[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$	1 340s, 1 300s, 1 280s, 1 190s, 910s, 902s	3 075w, 3 060m, 1 590w, 1 575w, 1 501m, 1 482m, 1 435s, 1 160m, 1 095s, 1 042w, 1 020w, 820s, 750m, 742m, 700vs, 635m
$[PdPh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)]$	1 340s, 1 290s, 1 190m, 912s	3 060m, 2 925w, 1 565s, 1 501m, 1 480m, 1 475m, 1 440s, 1 310m, 1 100s, 1 055m, 1 020m, 1 000w, 830m, 800w, 750s, 699vs, 640m
$[RhCl_2(NO)(PPh_3)_2]$		1 630vs (NO)
$[RuCl_3(NO)(PPh_3)_2]$		1 860vs (NO)

bonyl $[Rh(CO)\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)]$ was formed, and this could also be prepared by reaction of $[Rh(CO)_2\{ONN(R)O\}]$ with PPh_3. However, in none of these reactions was degradation of the $\{\overline{RhONN(R)O}\}$ ring observed. Similar treatment of $[Rh(\eta\text{-}C_5Me_5)Cl\{ONN(R)O\}]$ and $[Ru\{ONN(R)O\}_2(PPh_3)_2]$ also failed to cause break-up of the $\{\overline{MONN(R)O}\}$ ring, and so it would appear that PPh_3 is not responsible for the formation of nitrosyl species from these complexes.

Reaction of $[Rh\{ONN(R)O\}(PPh_3)_2]$ with iodine afforded two complexes, depending on the nature of R. When R = Ph, the species $[RhI_2\{ONN(Ph)O\}(PPh_3)_2]$, which appears to be a conventional oxidative-addition adduct, was formed. When R = C_6H_4Me-*p*, however, a compound whose analytical data were consistent with the formulation $[RhI\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ was isolated. Because of the compound's insolubility and involatility, we were unable to obtain spectroscopic information which could confirm the formulation. The compound could be binuclear, with a Rh–Rh bond and/or Rh–I–Rh bridges. However, iodine, as a relatively mild oxidising agent, is clearly not capable of decoupling the N–N bond in $[ONN(R)O]^-$.

When $[Rh\{ONN(R)O\}(PPh_3)_2]$ was treated with $RhCl_3 \cdot 3H_2O$ in ethanol at room temperature, $[RhCl_2\{ONN(R)O\}(H_2O)(PPh_3)]$ was formed. The nature of these species was firmly established by an *X*-ray crystallographic study of the compound where R = C_6H_4Me-*p* (see below).

We also noted that $[Ru\{ONN(R)O\}_2(PPh_3)_2]$ reacted similarly with $RuCl_3 \cdot 3H_2O$ in methanol giving the ruthenium(III) complexes $[RuCl\{ONN(R)O\}_2(PPh_3)_2]$. The formation of these species must presumably arise *via* ligand exchange but the metal–chelate ring appears to remain intact.

However, when $[PdPh\{ONN(R)O\}(PPh_3)]$ was treated with concentrated aqueous HCl at 80—90 °C both the phenyl and chelate ring were lost, and $[Pd_2Cl_4(PPh_3)_2]$ was isolated. No attempt was made to identify the fate of the nitrogen-containing fragments of this reaction.

Treatment of $[Rh\{ONN(C_6H_4Me\text{-}p)O\}(PPh_3)_2]$ with concentrated aqueous HCl in refluxing ether over 3 h afforded $[RhCl_2(NO)(PPh_3)_2]$ which was identified by analytical methods and by comparison (i.r. spectra, mixed m.p.) with an authentic sample. Similar treatment of $[Ru\{ONN(C_6H_4Me\text{-}p)O\}_2(PPh_3)_2]$ afforded $[RuCl_3(NO)(PPh_3)_2]$. Both the nitrosyl complexes were formed in high yields (92 and 87%, respectively). It would appear, therefore, that the occurrence of nitrosyl complexes during attempts to prepare Cupferron complexes of Rh^I and Ru^{II} may have been due to the presence of traces of acid in the reaction mixtures. The occurrence of $[Rh(NO)(PPh_3)_3]$ in reactions involving $[Rh\{ONN(R)O\}(PPh_3)_2]$ may be explained by reduction of $[RhCl_2(NO)(PPh_3)_2]$ either by PPh_3 released from $[RhCl(PPh_3)_3]$ in the formation of the Cupferron complex, or by the Cupferron complex itelf. Traces of $[Rh(NO)(PPh_3)_3]$ can be detected in direct reactions involving these species.

The organic products of the acid decomposition of $[M\{ONN(C_6H_4Me\text{-}p)O\}_x(PPh_3)_2]$ (M = Rh, $x = 1$; M = Ru, $x = 2$) were identified using a combination of gas chromatographic (g.c.) and g.c.–mass spectrometric (m.s.) techniques. These were *p*-nitrosotoluene, *p*-toluidine, and chlorotoluidine. *p*-Toluidine was the main component of the three, and only very small amounts of chlorotoluidine, probably a mixture of isomers, were detected. The overall yield of these compounds in the rhodium system was 45—50% of the theoretical value, and lower yields were obtained from the ruthenium complex. We were not able to detect any other organic compounds in the reaction mixture. The relatively low yield of organonitrogen products may be due to deficiencies in the work-up procedure or to variability in the reaction conditions leading to incomplete degradation of the $\overline{MONN(R)O}$ ring. In proposing a mechanism for the formation of the nitrosyl complexes and the organonitrogen products, we suggest that protonation of the $\overline{MONN(R)O}$ ring occurs first, followed by N–N bond cleavage and formation of an arylhydroxylamine as an intermediate [equations (1) and (2)]. We did not detect

$$[Rh\{ONN(R)O\}(PPh_3)_2] + 2HCl \longrightarrow [RhCl_2(NO)(PPh_3)_2] + RNHOH \quad (1)$$

$$[Ru\{ONN(R)O\}_2(PPh_3)_2] + 4HCl \longrightarrow [RuCl_3(NO)(PPh_3)_2] + RNHOH + (NOCl) \quad (2)$$

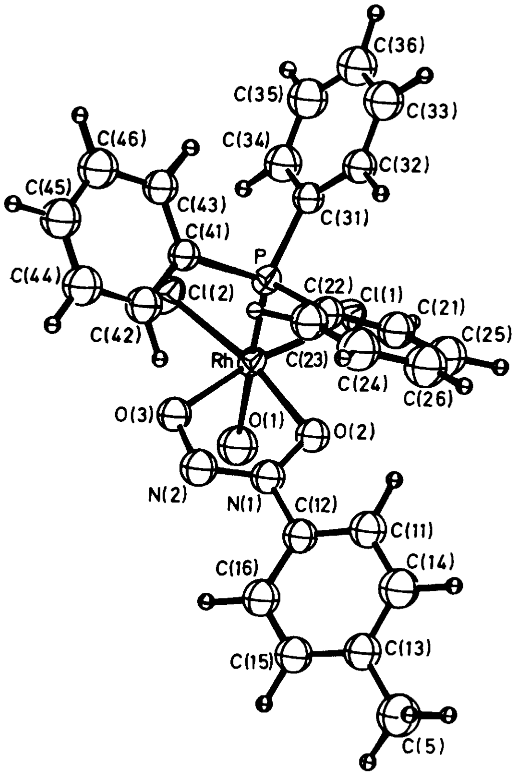


Figure. The molecular structure of $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]$ showing the atom numbering, with 50% thermal ellipsoids

p-tolylhydroxylamine in the reaction mixture but this might reflect the rapidity with which it is converted into other products under the conditions of the reaction and in the presence of transition-metal species.

Thus, phenylhydroxylamine is known[13] to react with HCl in alcohols to give aniline, chloroaniline, and other products. In the absence of air at room temperature, *p*-tolylhydroxylamine is converted into *p*-nitrosotoluene and *p*-toluidine [equation (3)].

$$2RNHOH \longrightarrow RNO + RNH_2 + H_2O \qquad (3)$$

Although this reaction is usually slow (of the order of days), it may be accelerated by transition-metal species and/or heat. It is conceivable that the toluidine derivatives could arise from *p*-nitrosotoluene, generated by scission of the N–N bond in the $\{\overline{MONN(R)O}\}$ ring. *p*-Nitrosotoluene is known[10] to be reduced in the presence of high concentrations of HCl, giving *p*-toluidine and chlorotoluidines. However, we feel that this route is less likely than that *via* *p*-MeC_6H_4NHOH, principally because reduction of *p*-MeC_6H_4NO requires higher concentrations of HCl than were present in the reactions described herein, and because the $\{\overline{MONN(R)O}\}$ ring seems remarkably stable *except* in the presence of HCl. Put another way, the Cupferron species were stable to nucleophiles under conditions which might have been expected to lead to elimination of *p*-MeC_6H_4NO, *e.g.* as in equation (4).

$$[Rh\{ONN(R)O\}(PPh_3)_2] + PPh_3 \longrightarrow [Rh(NO)(PPh_3)_3] + RNO \qquad (4)$$

An alternative mechanism for the formation of the nitrosyl and organonitrogen species might involve oxidative addition of HCl to the rhodium(I) species, giving $[RhCl(H)\{ONN(R)O\}(PPh_3)_2]$. Our experiments with I_2 confirmed that such a type of reaction could occur and it cannot be ruled out in this case. However, a similar reaction with the ruthenium complex, while not impossible, seems less likely.

Table 4. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Co-ordination sphere

Rh–Cl(1)	2.319(1)	Rh–O(1)	2.202(3)
Rh–Cl(2)	2.338(1)	Rh–O(2)	2.033(3)
Rh–P	2.250(1)	Rh–O(3)	2.019(3)
Cl(1)–Rh–Cl(2)	94.0(1)	O(2)–Rh–O(3)	80.4(1)
Cl(1)–Rh–P	91.4(1)	O(2)–Rh–P	94.2(1)
Cl(2)–Rh–P	92.8(1)	O(3)–Rh–P	94.7(1)
Cl(1)–Rh–O(1)	89.2(1)	O(2)–Rh–O(1)	83.9(1)
Cl(2)–Rh–O(1)	89.0(1)	O(3)–Rh–O(1)	84.4(1)
O(2)–Rh–Cl(1)	92.9(1)	O(3)–Rh–Cl(1)	91.9(1)

(*b*) Triphenylphosphine ligand

P–C(22)	1.839(4)	min. C–C	1.359(8)
P–C(31)	1.827(4)	max. C–C	1.425(8)
P–C(41)	1.825(4)	mean C–C	1.393(8)
Rh–P–C(22)	109.7(1)	min. P–C–C	117.1(3)
Rh–P–C(31)	117.2(1)	max. P–C–C	123.7(4)
Rh–P–C(41)	113.5(1)	mean P–C–C	120.4(3)
C(22)–P–C(31)	103.9(2)	min. C–C–C	117.9(4)
C(22)–P–C(41)	106.9(2)	max. C–C–C	121.9(6)
C(31)–P–C(41)	104.9(2)	mean C–C–C	120.6(5)

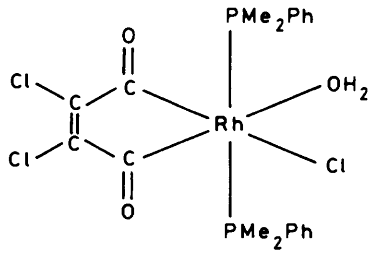
(*c*) $[ONN(C_6H_4Me\text{-}p)O]^-$ ligand

O(2)–N(1)	1.346(5)	C(5)–C(13)	1.527(7)
O(3)–N(2)	1.319(5)	min. C–C	1.387(7)
N(1)–N(2)	1.275(5)	max. C–C	1.404(7)
N(1)–C(12)	1.444(6)	mean C–C	1.394(7)
Rh–O(2)–N(1)	106.5(2)	C(5)–C(13)–C(14)	118.8(5)
Rh–O(3)–N(2)	112.6(3)	C(5)–C(13)–C(15)	122.2(5)
O(3)–N(2)–N(1)	115.4(4)	min. C–C–C	116.9(5)
N(1)–C(12)–C(11)	119.3(4)	max. C–C–C	122.7(5)
N(1)–C(12)–C(16)	118.0(4)	mean C–C–C	120.0(5)

Structure of $[RhCl_2\{ONN(C_6H_4Me\text{-}p)O\}(H_2O)(PPh_3)]\cdot 0.5Me_2CO$.—The *X*-ray study has established the identity of the complex. The asymmetric unit consists of a molecule of the complex and half a solvent molecule of crystallisation (Figure). Selected bond lengths and angles are given in Table 4.

The co-ordination geometry of the rhodium(III) atom is octahedral, with distortions produced by the various ligands. The two chlorine ligands are in *cis* positions, opposite the chelating $[ONN(C_6H_4Me\text{-}p)O]^-$ ligand. The water molecule and triphenylphosphine group complete the co-ordination in positions *trans* to one another. The geometries of the triphenylphosphine and $[ONN(C_6H_4Me\text{-}p)O]^-$ ligands are unremarkable, that of the latter being very similar to that of the corresponding $[ONN(Ph)O]^-$ in the iron complex.[4] The acetone molecule may be involved in hydrogen bonding with the co-ordinated water molecule since the only significant intermolecular interaction is O(1)···O(s1) at 2.74 Å.

A useful comparison can be made with the structure[14] of the rhodacyclopentenedione complex $[RhCl(H_2O)(PMe_2Ph)_2(C_4O_2Cl_2)]$ (**2**). Thus the distances Rh–P 2.250(1), Rh–O(H_2O) 2.202(3), and Rh–Cl 2.319(1) and 2.338(1) Å in the present complex are all shorter than the corresponding distances of 2.35, 2.28, and 2.50 Å respectively (no estimated standard deviations given) in the reference compound. This shortening can be rationalised in terms of the strong *trans* influence in the



(2)

reference compound of the Rh–C bonds opposite the Rh–O(H_2O) and Rh–Cl bonds, and the Rh–P bonds opposite to each other.

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