Deoxygenation Reaction of 2-Nitrophenol. Synthesis and *X*-Ray Crystal Structure of $[\overline{\mathrm{Ru(OC_6H_4N}}\mathrm{O}\text{-}o)(\mathrm{OC_6H_4NO_2}\text{-}o)(\mathrm{CO})(\mathrm{PPh_3})_2]$ †

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By reaction of $[\mathrm{Ru(CO)_3(PPh_3)_2}]$ with 2-nitrophenol, the deep brown ruthenium(II) complex, $[\overline{\mathrm{Ru(OC_6H_4N}}\mathrm{O}\text{-}o)(\mathrm{OC_6H_4NO_2}\text{-}o)(\mathrm{CO})(\mathrm{PPh_3})_2]$, has been obtained. *X*-Ray crystallography has shown that the complex contains a *o*-nitrosophenolate ligand, which co-ordinates to ruthenium in a chelating fashion through its nitroso-nitrogen and phenolic oxygen atoms.

The reduction of organic nitro-compounds by carbon monoxide bound to a transition-metal complex has been investigated in considerable detail. Interest in this reaction arises both from the unusual nature of the products which can be obtained in this way,[1] and by the practical importance of the reduction of the nitro-group by carbon monoxide for the synthesis of important chemicals.[2] Owing to our interest in the chemistry and in the catalytic and structural aspects of the metal–nitrogen bond,[3] we have started a study on the reactivity of 2-nitrophenol and related molecules with transition-metal complexes having CO and $\mathrm{PPh_3}$ as potential reducing agents of the nitro-group. The phenolic oxygen in the *ortho* position, being intrinsically a donor atom, should favour the reduction of the nitro-group by the surrounding ligands. We report here on the synthesis and *X*-ray crystal structure of the complex $[\overline{\mathrm{Ru(OC_6H_4N}}\mathrm{O}\text{-}o)(\mathrm{OC_6H_4NO_2}\text{-}o)(\mathrm{CO})(\mathrm{PPh_3})_2]$, obtained from the reaction of $[\mathrm{Ru(CO)_3(PPh_3)_2}]$ with 2-nitrophenol.

Experimental

$[\mathrm{Ru(CO)_3(PPh_3)_2}]$ was prepared as described in the literature,[4] while 2-nitrophenol was a commercial product. Infrared spectra were recorded on a Beckman 4210 i.r. spectrophotometer and on a Nicolet MX-1 FT-IR spectrometer. Carbon-13 and ^{31}P n.m.r. spectra were recorded on a Brucker VP-80 spectrometer, with $\mathrm{SiMe_4}$ as internal standard and 85% $\mathrm{H_3PO_4}$ as external standard, respectively. Elemental analyses were carried out in the analytical laboratories of Milan University.

$[\overline{\mathrm{Ru(OC_6H_4N}}\mathrm{O}\text{-}o)(\mathrm{OC_6H_4NO_2}\text{-}o)(\mathrm{CO})(\mathrm{PPh_3})_2]$.—To $[\mathrm{Ru(CO)_3(PPh_3)_2}]$ (0.2 g, 2.82 mmol) and 2-nitrophenol (0.117 g, 8.42 mmol), benzene (20 cm^3) degassed with dinitrogen was added. The solution was refluxed under a nitrogen atmosphere and with magnetic stirring. After 5 h the green-black solution was evaporated to *ca.* half the volume and by addition of n-hexane a dark brown compound precipitated out. This was filtered off and washed with n-hexane. Crystallization from benzene–n-hexane gave a deep brown, microcrystalline product which was dried *in vacuo*, m.p. = 180 °C (decomp.) (Found: C, 64.5; H, 4.4; N, 3.0. $\mathrm{C_{49}H_{38}N_2O_6P_2Ru}$ requires C, 64.4; H, 4.2; N, 3.1%). I.r. spectrum (Nujol mull): $\nu(\mathrm{CO})$ = 1 968, $\nu_{\mathrm{asym}}(\mathrm{NO_2})$ = 1 540, $\nu_{\mathrm{sym}}(\mathrm{NO_2})$ = 1 320, and $\nu(\mathrm{NO})$ = 1 340 cm^{-1}. ^{31}P N.m.r. spectrum ($\mathrm{CDCl_3}$): δ 22.7 p.p.m. (singlet). ^{13}C N.m.r. spectrum ($\mathrm{CDCl_3}$): δ 177.5 (CO), several signals between 110 and 140 p.p.m. (aromatics). Crystals suitable for the *X*-ray structure determination were obtained by slow diffusion of n-hexane into a benzene solution of the complex.

Table 1. Relevant bond distances (Å) and angles (°)

Ru–P(1)	2.419(1)	Ru–O(3)	2,080(2)
Ru–P(2)	2.412(1)	Ru–N(2)	1.961(3)
Ru–O(1)	2.129(2)	Ru–C	1.844(4)
		C–O	1.152(4)
N(2)–O(2)	1.246(4)	P(1)–Ru–P(2)	171.64(3)
N(2)–C(12)	1.412(5)	O(1)–Ru–O(3)	98.11(10)
C(7)–C(12)	1.378(5)	O(3)–Ru–N(2)	80.58(11)
C(7)–O(3)	1.306(4)	N(2)–Ru–C	89.94(13)
C(1)–O(1)	1.300(4)	C–Ru–O(1)	91.34(12)
N(1)–O(4)	1.220(5)	Ru–C–O	173.84(31)
N(1)–O(5)	1.223(5)		

In one preparation a red-violet complex was also obtained, which showed no absorptions in the i.r. spectrum at 1 540 cm^{-1} and with only one band in the 1 300—1 350 cm^{-1} region, thus suggesting that no nitro-groups were present in the molecule. However, many attempts to grow crystals suitable for an *X*-ray structure determination were unsuccessful; moreover the preparation of this material was not reproducible.

Crystal Data.—$\mathrm{C_{52}H_{41}N_2O_6P_2Ru}$, M = 952.93, triclinic, space group $P\bar{1}$, a = 10.525(2), b = 10.818(2), c = 20.915(8) Å, α = 86.53(2), β = 83.53(2), γ = 72.21(2)°, U = 2 252(1) Å^3, Z = 2, D_c = 1.405 g cm^{-3}, $F(000)$ = 978, $\mu(\text{Mo-}K_\alpha)$ = 4.61 cm^{-1}. Intensity data were collected on a Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å) in the θ range 3—25°. The structure, solved by conventional Patterson and Fourier methods using 4 876 absorption-corrected reflections with $I \geqslant 3\sigma(I)$, was refined by full-matrix least squares down to

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† Carbonyl(*o*-nitrophenolato-*O*)(*o*-nitrosophenolato-*N*,*O*)bis(triphenylphosphine)ruthenium(II).

Supplementary data available (No SUP 23842, 27 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 2. Positional parameters with estimated standard deviations in parentheses

Atom	x	y	z
Ru	0.487 01(4)	0.164 32(4)	0.225 30(2)
P(1)	0.483 1(1)	0.079 1(1)	0.334 89(7)
P(2)	0.480 5(1)	0.280 1(1)	0.122 90(7)
O	0.322 7(4)	0.002 6(4)	0.188 5(2)
O(1)	0.316 3(4)	0.321 8(3)	0.255 4(2)
O(2)	0.650 5(4)	−0.082 7(4)	0.174 4(2)
O(3)	0.634 5(3)	0.246 4(3)	0.242 2(2)
O(4)	−0.006 3(6)	0.579 0(6)	0.207 8(3)
O(5)	0.038 3(5)	0.402 7(5)	0.265 9(3)
N(1)	0.061 1(5)	0.502 9(5)	0.245 4(3)
N(2)	0.646 8(4)	0.022 7(4)	0.196 7(2)
C	0.379 5(5)	0.070 1(5)	0.203 7(3)
C(1)	0.296 0(6)	0.439 7(5)	0.273 6(3)
C(2)	0.392 3(6)	0.482 5(6)	0.299 4(3)
C(3)	0.363 9(7)	0.609 4(7)	0.318 0(4)
C(4)	0.242 5(8)	0.699 1(8)	0.309 5(4)
C(5)	0.145 9(7)	0.666 1(7)	0.284 8(3)
C(6)	0.171 4(6)	0.535 3(6)	0.269 2(3)
C(7)	0.754 0(5)	0.167 6(5)	0.225 9(3)
C(8)	0.872 1(6)	0.203 5(6)	0.230 8(3)
C(9)	0.993 5(7)	0.114 0(7)	0.215 0(4)
C(10)	1.006 0(7)	−0.006 4(7)	0.194 1(4)
C(11)	0.894 4(7)	−0.045 0(6)	0.186 6(3)
C(12)	0.769 3(6)	0.046 4(5)	0.203 3(3)
C(13)	0.063 4(9)	0.435 4(9)	0.446 0(5)
C(14)	0.096(1)	0.540 0(9)	0.462 1(5)
C(15)	−0.030(1)	0.392(1)	0.481 7(5)
C(111)	0.325 6(5)	0.052 3(5)	0.367 5(3)
C(112)	0.321 8(6)	−0.039 9(6)	0.416 4(3)
C(113)	0.200 4(7)	−0.057 7(7)	0.441 1(3)
C(114)	0.085 2(7)	0.013 3(7)	0.417 2(3)
C(115)	0.086 5(7)	0.105 8(6)	0.370 1(3)
C(116)	0.206 4(6)	0.124 8(6)	0.344 5(3)
C(121)	0.515 6(6)	0.182 4(6)	0.392 9(3)
C(122)	0.423 6(7)	0.233 7(6)	0.444 0(3)
C(123)	0.452 8(8)	0.313 5(8)	0.486 7(4)
C(124)	0.572 2(8)	0.339 2(8)	0.478 5(4)
C(125)	0.663 2(8)	0.293 0(8)	0.427 4(4)
C(126)	0.636 0(7)	0.212 6(7)	0.384 3(3)
C(131)	0.606 8(6)	−0.079 7(5)	0.345 7(3)
C(132)	0.706 0(7)	−0.100 2(7)	0.388 0(4)
C(133)	0.798 3(8)	−0.225 1(8)	0.391 9(4)
C(134)	0.790 9(8)	−0.321 6(8)	0.356 4(4)
C(135)	0.694 1(7)	−0.303 5(7)	0.316 8(4)
C(136)	0.600 3(6)	−0.180 3(6)	0.310 7(3)
C(211)	0.614 6(5)	0.198 7(5)	0.062 5(3)
C(212)	0.614 3(7)	0.076 8(6)	0.045 1(3)
C(213)	0.716 3(8)	0.003 1(8)	0.000 4(4)
C(214)	0.817 8(8)	0.051 8(8)	−0.022 7(4)
C(215)	0.819 3(8)	0.172 8(8)	−0.007 9(4)
C(216)	0.714 9(7)	0.250 6(7)	0.035 9(3)
C(221)	0.492 4(6)	0.442 9(5)	0.130 6(3)
C(222)	0.611 0(6)	0.459 5(6)	0.148 4(3)
C(223)	0.616 2(7)	0.585 3(7)	0.158 1(3)
C(224)	0.509 2(7)	0.686 0(7)	0.152 0(4)
C(225)	0.393 9(7)	0.674 7(7)	0.135 7(4)
C(226)	0.382 6(7)	0.550 5(6)	0.124 6(3)
C(231)	0.328 5(5)	0.306 1(5)	0.083 2(3)
C(232)	0.211 3(6)	0.304 3(6)	0.118 1(3)
C(233)	0.094 4(7)	0.327 9(7)	0.088 3(3)
C(234)	0.096 8(7)	0.350 4(7)	0.024 0(4)
C(235)	0.212 1(7)	0.352 6(7)	−0.011 8(4)
C(236)	0.329 0(7)	0.330 3(6)	0.017 6(3)

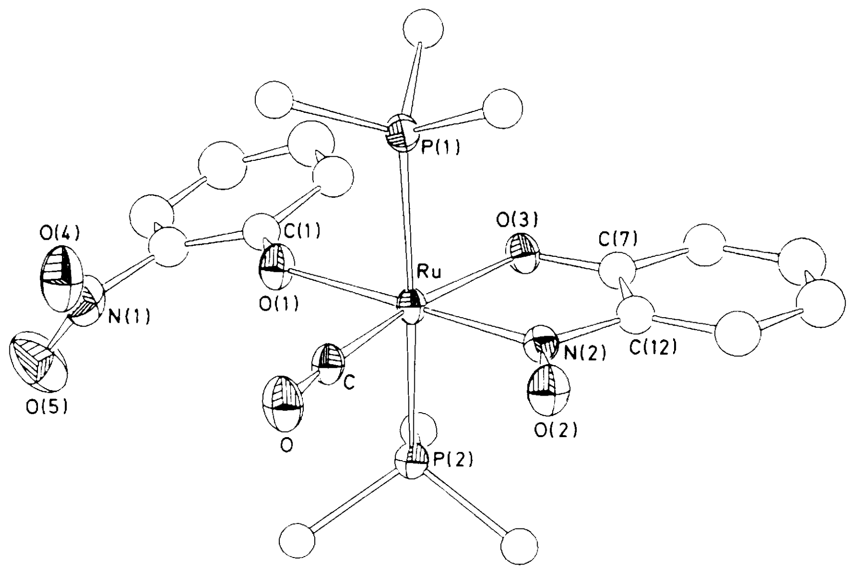

Figure. ORTEP view of [Ru(OC$_6$H$_4$NO-*o*)(OC$_6$H$_4$NO$_2$-*o*)(CO)(PPh$_3$)$_2$]; only the first carbon atoms of the triphenylphosphine phenyl rings are represented for clarity

R = 0.053 and R' = 0.073. Hydrogen atoms in their calculated positions were introduced in the last cycles of the refinement. Relevant bond lengths and angles within the complex molecule are reported in Table 1 and atomic co-ordinates in Table 2.

Results and Discussion

By reaction in refluxing benzene of [Ru(CO)$_3$(PPh$_3$)$_2$] with 2-nitrophenol, the brown complex, [Ru(OC$_6$H$_4$NO-*o*)(OC$_6$H$_4$-NO$_2$-*o*)(CO)(PPh$_3$)$_2$], has been obtained. The i.r. spectrum of this compound shows bands due to a nitro-group, in addition to an absorption at 1 340 cm^{-1}, attributable to a nitroso-group bound *via* the nitrogen atom.[5] The ^{31}P n.m.r. spectrum showed only one signal, suggesting a similar chemical environment for the two phosphine ligands. In order to establish the real nature of this complex, we have carried out a single-crystal *X*-ray determination. The present compound crystallizes with clathrate benzene molecules, the ratio between the complex molecule and the solvent being 2 : 1. As can be seen in the Figure the Ru atom is in a distorted octahedral environment with the two triphenylphosphine ligands *trans* to each other in an almost eclipsed conformation. The bond angles about the metal atom range from 80.6(1) to 98.1(1)°. The *o*-nitrosophenolate ligand is co-ordinated in a chelating fashion, through its nitroso-nitrogen and phenolic oxygen atoms, similar to that found in the 1 : 1 pyridine adduct of (4-methyl-1-benzoquinone 2-oximato)copper(II) [6] and in the anion tris(4-chloro-1-benzoquinone 2-oximato)niccolate(II).[7] The *o*-nitrophenolate anion acts as a monodentate ligand *via* its phenolic oxygen, whereas in some cobalt and copper complexes, such as $[Co(mim)_2(OC_6H_4NO_2\text{-}o)_2]$ (mim = *N*-methylimidazole),[8] $[Cu(PPh_3)_2(OC_6H_4NO_2\text{-}o)]$, and $[Cu(PPh_3)_2\{OC_6H_3(NO_2)_2\text{-}2,4\}]$,[9] a chelating co-ordination mode is observed.

It is interesting that the NO_2 group is not coplanar with the phenyl ring of the nitrophenolate anion (dihedral angle between the planes of the NO_2 moiety and the phenyl ring 43.4°). The planarity of the ligand, which would allow a strong delocalization to take place, is destroyed in order to preserve a series of correct non-bonding interactions with the hydrogen atoms of the triphenylphosphine ligands.

The nitroso-group is shielded from further reduction by formation of the complex. On the other hand the reduction of the second nitro-group is probably disfavoured by the new oxidation state of ruthenium.

The reduction of nitrobenzene in the presence of pentacarbonyliron is known to occur by photochemical or radiochemical activation.[10] We have found that $[Fe(CO)_3(PPh_3)_2]$, unlike $[Ru(CO)_3(PPh_3)_2]$, does not react thermally with 2-nitrophenol. Thus ruthenium complexes appear to be more suitable compounds for studies on the reactivity of nitrophenols.

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