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An example of a nitrogen-bonded arylnitroso complex. The crystal structure of RhCl(NBD)(p-BrC_6H_4NO)

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Abstract

The crystal structure of RhCl(NBD)(p-BrC_6H_4NO) has been determined by an X-ray diffraction study. The nitroso ligand is σ-(N) bonded, and the complex crystallizes in the triclinic space group $P\bar{1}$ with a 7.667(4), b 9.373(4), c 9.611(3) Å, α 94.81(2), β 94.37(1), γ 96.40(3)°, V 681.4(5) Å^3 and $Z = 2$. Final R and R_w indices are 0.0486 and 0.0573 for 1754 observed reflections. A correlation was found between the values of $\Delta\nu$ ($\nu(N{-}O)_{complex} - \nu(N{-}O)_{free\ ligand}$) and the bonding mode of the nitroso ligands.

Introduction

It is well established that arylnitroso ligands can coordinate to the metal by various bonding modes, such as: (a) σ-(N) [1,2,3], (b) σ-(O) [4], (c) η^2-(NO) [5], (d) η^2-(NO), σ-(N) [6] (e), 2σ-(N) [7], (f) σ-(N), σ-(O) [7]. A correlation between the bonding mode and the ν(N–O) stretching frequency has not been established for the synthesis of many arylnitroso complexes, only a few of which, however, have been subjected to X-ray diffraction study. Recently we reported the preparation and the spectroscopic properties of several arylnitroso complexes of Rh^I, Ir^I, Ru^{II}, Pd^{II} and Pt^{II} [8,9]. In addition to this we have determined the molecular structure of some of these complexes and based on this we propose a criterion for distinguishing between some different bonding modes of the nitroso ligand.

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Experimental

The nitroso complex $RhCl(NBD)(p\text{-}BrC_6H_4NO)$ (NBD = norbornadiene) was prepared as previously reported [8]. Violet air-stable crystals were obtained by slow diffusion of diethyl ether into a saturated acetone solution of the complex.

The compound ($C_{13}H_{12}BrClNORh$, $M = 416.506$) crystallizes in the triclinic space group $P\bar{1}$ with a 7.667(4), b 9.373(4), c 9.611(3) Å, α 94.81(2), β 94.37(1), γ 96.40(3)°, V 681.4(5) Å^3, $Z = 2$, μ(Mo-K_α) 4.323 mm^{-1}, D_c 2.030 Mg m^{-3}, $F(000)$ 404, T 295 K. A crystal with dimensions 0.07 × 0.10 × 0.30 mm was used for the data collection. The three dimensional intensity data were collected for θ values between 2.5° and 27.0° on a Siemens AED diffractometer by the θ–2θ scan technique using Nb-filtered Mo–K_α radiation. No decomposition of the crystal was detected during the data collection. A total of 2972 reflections were measured, of which 1754 were considered as observed ($I \geqslant 2\sigma(I)$). The data were corrected for Lorentz, polarization, and absorption effects (the maximum and minimum transmission factors were 1.1592 and 0.8599, respectively [10,11]).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares with the SHELX system of programs [12]. All non-hydrogen atoms were refined anisotropically. A final difference Fourier treatment revealed the positions of all the hydrogen atoms, but three aryl hydrogens were successively located in their calculated positions and all were introduced in the final structure factor calculation. At convergence: $R = 0.0486$, $R_w = 0.0573$, ($R_w = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2}$, $w = k[\sigma^2(F_o) + g\,F_o^2]^{-1}$, $k = 1.0000$, $g = 0.001560$).

The fractional atomic coordinates for non-hydrogen atoms are given in Table 1. Complete tables of bond lengths and angles, thermal parameters for non-hydrogen atoms, the H coordinates, and a list of observed and calculated structure factors are available from the authors.

Table 1

Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms, with esd's in parentheses

Atom	x	y	z	B_{eq}
Rh	892(1)	657(1)	2462(1)	2.72(2)
Br	3977(2)	5869(1)	8283(1)	7.06(5)
Cl	−1953(3)	485(2)	3247(3)	3.65(7)
O	917(11)	3529(8)	1707(8)	5.97(25)
N	1204(10)	2779(8)	2674(8)	3.65(22)
C(1)	1866(11)	3577(9)	3976(9)	2.97(23)
C(2)	2238(12)	2782(9)	5101(10)	3.55(25)
C(3)	2852(12)	3462(10)	6382(10)	3.78(27)
C(4)	3103(12)	4953(10)	6523(10)	4.00(28)
C(5)	2728(14)	5761(10)	5423(11)	4.16(29)
C(6)	2101(14)	5078(10)	4136(11)	4.22(29)
C(7)	769(12)	−1542(10)	1511(10)	3.61(26)
C(8)	1459(12)	−1468(9)	2896(10)	3.32(25)
C(9)	3441(11)	−1142(10)	2879(9)	3.52(26)
C(10)	3587(12)	389(9)	2492(11)	3.87(28)
C(11)	2853(12)	341(12)	1106(11)	4.57(32)
C(12)	2281(14)	−1254(12)	631(9)	4.44(31)
C(13)	3716(13)	−1987(12)	1480(10)	4.61(31)

Results and discussion

The structure of the complex is shown in Fig. 1, and selected bond distances and angles are listed in Table 2. The rhodium atom has a square-planar coordination with a slight tetrahedral deformation. The *p*-bromophenylnitroso ligand acts as a monodentate ligand through N, and the coordination at Rh is completed by a chlorine atom and the midpoints of the two olefinic bonds of NBD. The *p*-bromophenylnitroso ligand is exactly planar, and is almost perpendicular to the coordination mean-plane (94.2(1)°), The structure shows two short H...O and H...Rh (H(6)...O 2.42, H(2)...Rh 2.67 Å) contacts. The Rh–M(1) and Rh–M(2) distances (2.05(1), 1.98(1) Å, respectively, M(1) and M(2) are the midpoints of the two olefinic bonds) are significantly different, and reflect the operation of a *trans* effect.

In Table 3 we show IR spectral data for some arylnitroso complexes along with the corresponding bonding modes. It will be seen that when the arylnitroso ligand coordinates through the nitrogen there is a lowering of the ν(N–O) stretching frequency whereas when it coordinates through the oxygen this frequency is increased. The X-ray structure of $CoCl_2(NODMA)_2$ [3] (which has the ν(N–O) band at 1498 cm^{-1}, 29 cm^{-1} lower than that of the free NODMA ligand, NODMA = 4-nitroso-*N*,*N*-dimethylaniline), which had been thought from the spectrum to be oxygen-bonded, revealed coordination of the arylnitroso ligand through the nitrogen atom. Such coordination was also observed for the *trans*-$PdCl_2(C_6H_5NO)_2$ [1], whereas crystal structure of $SnCl_2Me_2(NODMA)_2$ [4], (with

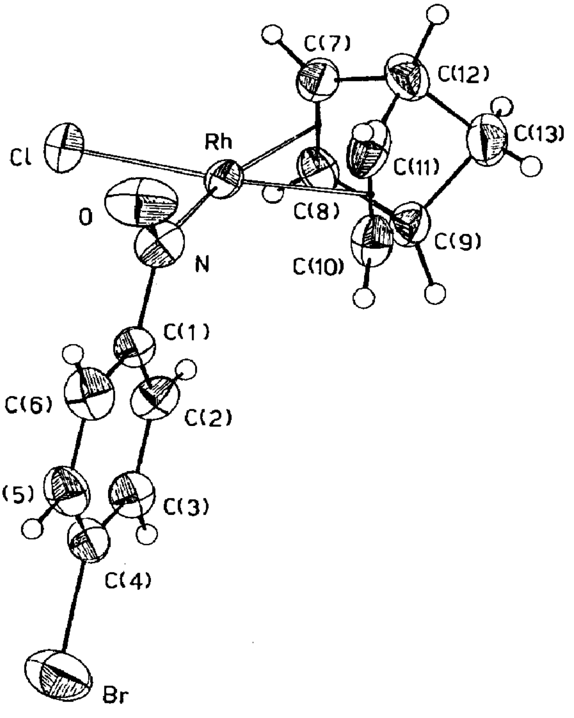

Fig. 1. View of the structure with the atomic numbering scheme (thermal parameters are drawn at the 40% probability level).

Table 2

Selected bond distances (Å) and angles (°) (with esd's in parentheses)

Rh–N	1.968(8)	Rh–M(1)	2.05(1)	N–O	1.23(1)
Rh–Cl	2.355(3)	Rh–M(2)	1.98(1)	N–C(1)	1.43(1)
N–Rh–Cl	93.8(2)	Cl–Rh–M(1)	97.7(3)	Rh–N–O	123.8(6)
N–Rh–M(1)	168.2(4)	Cl–Rh–M(2)	168.2(3)	Rh–N–C(1)	121.7(6)
N–Rh–M(2)	98.0(4)	M(1)–Rh–M(2)	70.5(4)	C(1)–N–O	114.4(7)

M(1) and M(2) are the midpoints of the C(7) = C(8) and C(10) = C(11) olefinic NBD bonds respectively.

the (N–O) band at 1563 cm^{-1}, 36 cm^{-1} higher than that of the free NODMA ligand) shows the coordination to be through the oxygen atom.

The coordination of the arylnitroso ligand through the η^2-N–O or η^2-N–O and σ-(N) bonds results in a large decrease of the ν(N–O) stretching frequency, much larger than that observed previously for complexes having the ligand predominantly single bonded [5b,14,15]. From Table 2 it can also be seen that a σ-(N) bonding mode seems likely for the complexes RhCl(COD)(p-BrC_6H_4NO) and IrCl(COD)(p-BrC_6H_4NO) (COD-cyclooctadiene), in which there is a fall in ν(N–O) upon coordination, similar to that observed in the σ-(N)-coordinated RhCl(NDB)(p-BrC_6H_4NO).

We thus think that there is a correlation between coordination mode and ν(N–O), but X-ray structural data for additional relevant complexes are needed to confirm it. In (μ-η^1-nitrosobenzene-*N*)(μ-η^2-nitrosobenzene-*N*,*O*)(η^1-nitrosobenzene-*N*)tris(trimethylphosphine)diplatinum(II) [7] there are three nitroso bonding modes and it is difficult to assign the single N–O stretching mode.

Table 3

IR spectra (cm^{-1}) of some arylnitroso complexes

Complex	ν(N–O) [a] (cm^{-1})	$\Delta\nu$ [b] (cm^{-1})	N–O bond length (Å)	bonding mode	Ref.
$SnCl_2Me_2(p\text{-}Me_2NC_6H_4NO)_2$	1563	+36	1.218(4)	σ-(O)	4
$CoCl_2(p\text{-}Me_2NC_6H_4NO)_2$	1498	−29	1.267(5)	σ-(N)	3
$PdCl_2(p\text{-}Me_2NC_6H_4NO)_2$	1505	−22		σ-(N) [d]	[e]
RhCl(NBD)(p-BrC_6H_4NO) [c]	1473	−32	1.23(1)	σ-(N)	this work
RhCl(COD)(p-BrC_6H_4NO) [c]	1465	−40		σ-(N) [d]	8
IrCl(COD)(p-BrC_6H_4NO) [c]	1473	−32		σ-(N) [d]	8
$PdCl_2(C_6H_5NO)_2$	1490	−15	1.209(3)	σ-(N)	1
RhCl(NBD)(C_6H_5NO) [c]	1483	−22		σ-(N) [d]	8
$PtCl_2(C_6H_5NO)_2$	1495	−10		σ-(N) [d]	9
$Pt(PPh_3)_2(C_6H_5NO)$	975	−530	1.410(7)	η^2-(NO)	5b
$[Pd(C_6H_5NO)(PBu^t_3)]_3$	1039	−466	1.35(1)	η^2-NO), σ-(N)	13,14
$[\{Co(cp)\}_2(\mu\text{-}C_6H_5NO)_2]$ [c]	1047	−458	1.385(4)	η^2-(NO), σ-(N)	15

[a] In Nujol mull. [b] Difference between the ν(N–O) of the complex and the ν(N–O) of the free ligand. [c] COD = cyclooctadiene, cp = cyclopentadienyl, NBD = norbornadiene. [d] Our assignment. [e] Our assignment, prepared by us.

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