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THE STRUCTURE OF THE NITROSYL [$RuCl_3(NO)(AsPh_3)_2$] COMPLEX

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Abstract—The structure of the title compound, [$RuCl_3(NO)(AsPh_3)_2$], has been determined by X-ray diffraction. The ruthenium atom is octahedrally coordinated with the arsine ligands in the *trans* configuration. The ν(NO) was found at 1869 cm^{-1} in the IR spectrum, which is consistent with the linearity of the Ru—N—O bond angle.

Nitric oxide is an odd electron molecule and structural and synthetic studies have shown that the reaction chemistry of this ligand is varied and interesting. This ligand reacts with a variety of transition-metal compounds to form nitrosyl complexes which can be a source of interest in part because the nitric oxide is able to bind to metal ions in enzymes reacting with dioxygen and can be used as a probe of dioxygen binding sites.[1] Indeed, nitrosyl has been shown to exist in both linear and bent forms corresponding to three-electron and one-electron donor ligands, respectively. Distinction between these two geometries in mononuclear nitrosyl complexes can be made by means of crystallographic and spectroscopic studies.[2] In this paper we report on the characterization and X-ray structure of the complex trichloronitrosyl-bis(triphenylarsine)ruthenium. Our aim was to provide a direct comparison of the nitrosyl group present in this complex with that found in the similar complex $RuCl_3(NO)(PPh_3)_2$.[3]

EXPERIMENTAL

$RuCl_3(NO)(AsPh_3)_2$ was synthesized from Ru Cl_3NO, which was prepared by a modified Fletcher method[4] of passing NO through a solution of commercial ruthenium chloride (Degussa S.A.) until the solution became red, followed by evaporation to a small bulk with hydrochloric acid. The NO was generated from dilute nitric acid (*ca* 33%) over copper metal. The NO gas was dried by passing it through a column containing anhydrous $CaCl_2$. The $RuCl_3(NO)(AsPh_3)_2$ was synthesized from a deoxygenated methanolic solution (10 cm^3) of nitrosylruthenium trichloride (0.1 g, 0.42 mol) and triphenylarsine (0.26 g, 0.85 mol) under reflux for 2 h. The yellow precipitate formed was filtered and washed with ether. Found: C, 50.4; H, 3.6; N,

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Table 1. Crystallographic and refinement data

Crystal data	
Space group	$C2/c$
a (Å)	24.7888(5)
b (Å)	9.5966(2)
c (Å)	15.9006(3)
α (°)	90
β (°)	116.95(2)
γ (°)	90
V (Å^3)	3371.59(3)
M_r	849.92
Z	4
D_x (mg m^{-3})	1674
λ (Mo-K_α) (Å)	0.70930
μ (cm^{-1})	26.7
Crystal dimensions approx. (mm)	$0.1 \times 0.2 \times 0.4$
Data collection	
Mode	ω–2θ
Scan rate (° min^{-1})	6.7–20
θ range (°)	0–25
Range of hkl	$-29 \leqslant h \leqslant 26, 0 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 18$
Total reflections measured	2749
Unique reflections	2637
$F(000)$	1688
Structure determination and refinement	
Reflections used [$I > 3\sigma(I)$]	1881
No. of variables	110
R, R_w	0.031, 0.031
Max. shift/e.s.d.	0.003
Max., min. density in final difference map (e Å^{-3})	0.35, −0.53
S	1.36
Max., min. absorption corr.	1.15, 0.84

1.8%. $C_{36}H_{30}NOCl_3As_2Ru$ requires: C, 50.9; H, 3.6; N, 1.7%.

Suitable crystals were grown by slowly diffusing ether into a concentrated solution of the complex in dichloromethane. The triphenylarsine and the $RuCl_3(NO)(dppe)$, $RuCl_3(NO)(en)$, $RuCl_3(NO)$ (o-phen) and $RuCl_3(NO)(py)_2$ [where dppe = 1,2-bis(diphenylphosphino)ethane; en = ethylenodiamine; o-phen = o-phenanthroline; py = pyridine] complexes which were characterized by microanalysis data were synthesized according to methods described in the literature.[5]

The IR spectra were measured from crystalline powder samples diluted in CsI on a Bomem-Michelson 102 spectrometer in the region 4000–190 cm^{-1}. A single crystal of approximate dimensions $0.1 \times 0.2 \times 0.4$ mm was used for data collection and cell parameter determination on an Enraf–Nonius CAD-4 diffractometer, with graphite monochromized Cu-K_α radiation at room temperature ($T = 25°C$). Unit-cell parameters were obtained by least-squares from the setting angles of 25 reflections. Intensity data were collected in the ω–2θ scan mode up to $\theta_{max} = 25°$ ($-29 \leqslant h \leqslant 26, 0 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 18$), with scan rates between 6.7 and 20° min^{-1}. The intensity of one standard reflection was essentially constant throughout the experiment. Of the 2637 independent reflections measured, 1881 had $I > 3\sigma(I)$ and were employed in the refinement procedure, which included 110 parameters. Data were corrected for Lorentz polarization and absorption effects, with maximum and minimum transmission factors of 1.15 and 0.84, respectively, using the method of Walker and Stuart.[6] The structure was solved using the heavy atom method and difference Fourier techniques. In the final cycles of least-squares refinement, all non-hydrogen atoms were treated anisotropically; all hydrogen atoms were then included as fixed contributors with one refined common isotropic temperature factor (0.067 Å^2). The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_0) + 0.00009F_0^2$, and the refinement converged to final $R = 0.031$, $R_w = 0.031$ and $S = 1.36$ [$S = (\Sigma w(|F_0| - |F_c|)^2/(M-N))^{1/2}$, where M = number of observations, N = number of refined parameters]. In the final refinement cycle, the maximum shift-to-e.s.d. ratio was 0.003 and the maximum and minimum electron densities in the difference map were 0.35 and −0.53 e Å^{-3}, respectively. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[7] with corrections for anomalous dispersion from Cromer and Liberman,[8] and for hydrogen atoms from Stewart *et al.*[9]

All calculations were performed with the program SHELX76.[10] The data collection and refinement parameters are summarized in Table 1. The relevant interatomic distances and angles are listed in Table 2. Figure 1 is a projection of the molecule showing the atom numbering scheme (drawn with the program ORTEP[11]).

Table 2. Selected interatomic distances (Å) and angles (°)

Ru—N	1.729(7)
Ru—Cl(1)	2.346(2)
Ru—Cl(2)	2.384(1)
Ru—As(1)	2.5198(6)
N—O	1.151(9)
As(1)—C(11)	1.931(6)
As(1)—C(12)	1.935(5)
As(1)—C(13)	1.929(6)
N—Ru—Cl(2)	90.0(1)
N—Ru—As(1)	91.5(1)
Cl(1)—Ru—Cl(2)	89.98(5)
Cl(1)—Ru—As(1)	88.45(3)
Cl(2)—Ru—As(1)	87.33(4)
Ru—N—O	180.0(3)
Ru—As(1)—C(11)	119.6(2)
Ru—As(1)—C(12)	106.9(2)
Ru—As(1)—C(13)	118.7(2)
C(11)—As(1)—C(12)	106.0(2)
C(11)—As(1)—C(13)	99.9(2)
C(12)—As(1)—C(13)	104.1(2)
As(1)—C(11)—C(21)	120.7(4)
As(1)—C(11)—C(31)	151.6(3)
As(1)—C(11)—C(51)	149.3(3)
As(1)—C(11)—C(61)	119.0(4)
As(1)—C(12)—C(22)	121.0(4)
As(1)—C(12)—C(32)	151.3(3)
As(1)—C(12)—C(52)	148.1(3)
As(1)—C(12)—C(62)	118.8(4)
As(1)—C(13)—C(23)	122.4(4)
As(1)—C(13)—C(33)	152.4(3)
As(1)—C(13)—C(53)	148.6(3)
As(1)—C(13)—C(63)	118.5(4)

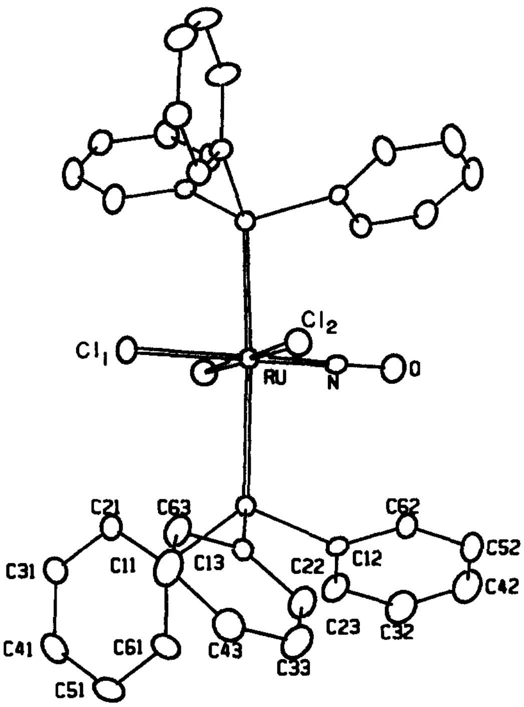

Fig. 1. The molecular structure of [$RuCl_3(NO)(AsPh_3)_2$].

RESULTS AND DISCUSSION

$RuCl_3(NO)(AsPh_3)_2$ belongs to the *C*2/*c* space group. The ruthenium, NO and chlorine species are sited on a crystallographic two-fold axis, therefore only half of the molecule is independently located in the asymmetric unit. Its structure consists of discrete and well-separated monomers and it is isomorphous with $RuCl_3(NO)(PPh_3)_2$ and $OsCl_3(NH_3)(PPh_3)_2$.[12] The three mutually perpendicular coordination planes are well defined. Their angles are close to 90°, showing almost no distortion in the molecule. The Ru—N—O bond angle of 180.0(3)° found in the triphenylarsine complex shows the linearity of the N—O group in this structure. These parameters are very similar to those found for $RuCl_3(NO)(PPh_3)_2$. The Ru—As distance [2.5198(6) Å] is longer than the Ru—P [2.465(1) Å] found for the triphenylphosphine complex. These data show that the bond lengths for Ru—P are shorter than those involving Ru—As, as expected, considering the different covalent radii of these atoms.[13] The N—O distance at 1.151(9) Å is near the distance found in the free ligand,[14] suggesting absence or very low backbonding in the bonding between the ruthenium and nitrogen atoms. The Ru—Cl(2) distance of 2.384(1) Å is essentially the same as other such distances in Ru^{III} phosphine complexes when chloride is *trans* to another chloride ligand.[15] The Ru—Cl(1), at 2.346(2) Å, is shorter than Ru—Cl(2) by about 0.04 Å as a result of its *trans* disposition to the nitrosyl ligand. The shortening of the metal–ligand bond *trans* to a linear nitrosyl ligand has been observed before,[16,17] even for $RuCl_3(NO)(PPh_3)_2$.[3] This indicates that the chlorine *trans* to the NO group is bonded more tightly to the metal, which is consistent with the fact that in some chemical reactions it remains intact.[18,19]

The IR spectrum of the $RuCl_3(NO)(AsPh_3)_2$ complex shows ν(NO) at 1869 cm^{-1}. This is consistent with the linear NO range of Haymore and Ibers[3] [ν(NO) above 1620–1610 cm^{-1} were assigned to linear M—N—O systems, while ν(NO) below 1610 cm^{-1} were assigned to bent M—N—O systems]. The complete linearities found in Ru—N—O for the triphenylarsine and triphenylphosphine complexes can explain the almost identical values for the ν(NO) found in these compounds. $RuCl_3(NO)(dppe)$, $RuCl_3(NO)(en)$, $RuCl_3(NO)(py)_2$ and $RuCl_3(NO)(phen)$, also synthesized from $RuCl_3(NO)$, show a ν(NO) very close to 1870 cm^{-1}, which is consistent with the same linearity of the NO group present in these complexes. The fascinating $[RuCl(NO)_2(PPh_3)_2]^+$ complex shows bands at 1845 and 1687 cm^{-1} in the IR spectrum. These bands were assignable to ν(NO) of the linear and the bent nitrosyl functions, respectively.[20] $OsCl_3(NO)(PPh_3)_2$ and $IrCl(NO)(PPh_3)_2^+$ show ν(NO) bands at 1850 and 1945 cm^{-1}, which are according to the linearities of the nitrosyl species in these molecules.[21] The IR spectra of *trans*-$[RuL(NO)(PMe_3)_2](ClO_4)_3$, where L is a 2,6-bis(pyrazol-1-yl)pyridine, show ν(NO) in the region 1910–1930 cm^{-1}, also suggesting a linear NO^+ group.[22]

Supplementary material

Isotropic thermal parameters, atom coordinates, complete list of bond distances and angles and the observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

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