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Synthesis, molecular and crystal structure of the zwitterionic Re(V)-oxo complex $ReOCl_3(L)(PPh_3)$ with L = 2-(diethylaminomethyl)-4-methylphenol

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Abstract

Ligand exchange between 2-(diethylaminomethyl)-4-methylphenol (N \cap OH) and ReOCl₃(PPh₃)₂ yields green crystals of the zwitterionic complex ReOCl₃(O \cap NH)(PPh₃). The X-ray diffraction study reveals that the structure consists of monomeric units in which the distorted octahedral coordination around Re is provided by the oxo group, the three Cl atoms in a *mer* arrangement, the PPh₃ ligand and the phenolate oxygen *trans* to the oxo group. The amino-phenol is monodentate via the phenolate oxygen, whereas the amine in the side-arm has been quaternized by migration of the phenol proton. The resulting ammonium group forms an intramolecular N-H…Cl hydrogen bond with an adjacent Cl ligand, making the complex highly resistant to deprotonation. The ¹H NMR spectra indicate that the N-H proton is not labile in CDCl₃. Electron delocalisation along the O=Re-O-C(phenolate) moiety via the sp-hybridised oxygen of the end-on coordinated phenolate would be consistent with the short Re-O(phenolate) distance of 1.915(3) Å observed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium-oxo system; Amino-phenol; Hydrogen bond; Crystal structures

1. Introduction

Schiff base complexes, particularly those obtained by condensation of salicylaldehyde with various amines, represent an important class of compounds in the coordination chemistry of Re(V)-oxo systems. This series of complexes are usually hexacoordinate, neutral or anionic, with a ligand composition and distribution depending on the reaction conditions [1]. On the other hand, (aminomethyl)phenol ligands, where the lack of unsaturated C=N bonds precludes electron delocalisation over a planar metallacycle, have not yet been reported to form Re-oxo complexes, in spite of the fact that they are known to coordinate to Cu(II) [2], Zn(II) [2,3], Ni(II) [4], W(VI) [5] and lan-thanide(III) [6] centres.

Our research group is currently investigating the chemistry of the Re=O complexes with various P,O-donor ligands (P O OH) [7–9], whose importance as models for radiopharmaceuticals is well known. This study is now being extended to 2-(dialkylamino-methyl)phenols. Here we wish to report on the reaction of 2 - (diethylaminomethyl) - 4 - methylphenol (N O OH) with ReOCl₃(PPh₃)₂, which gives a quantitative yield of ReOCl₃(O N NH)(PPh₃), a complex in which the ligand is coordinated in a monodentate fashion via oxygen, with the proton being shifted onto the amino nitrogen atom. This species of an unprecedented type in rhenium chemistry was characterised spectroscopically and its structure was determined by X-ray diffraction.

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2. Experimental

2.1. Materials and methods

2 - (Diethylaminomethyl) - 4 - methylphenol - (2 - Et₂-NCH₂-4-Me-C₆H₄OH (N O OH) [10] and ReOCl₃(PPh₃)₂ [11] were synthesised by procedures described in the literature.

IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on a Perkin–Elmer 1600 spectrophotometer. ¹H and ³¹P{¹H} NMR spectra were recorded in CDCl₃ at room temperature (r.t.) on a Bruker ARX 400 apparatus. For the ¹H spectra, the residual solvent signal ($\delta = 7.27$ ppm) was used as internal standard. For ³¹P{¹H} NMR, the external standard was H₃PO₄ (85%/D₂O, $\delta = 0.00$ ppm). Mass spectra were obtained with a



Scheme 1.

Table 1				
Crystallographic	data	and	experimental	details

Formula	C ₃₀ H ₃₄ Cl ₃ NO ₂ PRe
Formula weight	764.14
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	18.503(3)
b (Å)	9.172(2)
$c(\dot{A})$	20.030(5)
β(°)	117.81(2)
$V(Å^3)$	3006.7(11)
Z	4
Temperature (K)	220(2)
D_{calc} (g cm ⁻³)	1.688
Crystal size (mm)	$0.23 \times 0.17 \times 0.04$
Crystal shape and color	green plate
$\mu (\mathrm{mm}^{-1})$	3.50
2θ Range (°)	0–140
Unique data	5693
Observed data $[I > 2\sigma(I)]$	4420
Weighting scheme (w^{-1})	$[\sigma^2(F_o^2) + (0.0176P)^2]^a$
$R [I > 2\sigma(I)], R_1^{b}$	0.0295
wR_2	0.0664
R (all data), R_1^{b}	0.0434
wR_2	0.0694
Goodness-of-fit (S ^b)	0.969

^a $P = (F_{o}^{2} + 2F_{c}^{2})/3.$

^b $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|), wR_2 = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma (wF_o^2)^2]^{1/2}, S = [\Sigma w (F_o^2 - F_c^2)^2/(\text{no. of reflns.} - \text{no. of params.})]^{1/2}.$

NERMAG R10-10 mass spectrometer using the FAB (MNBA) technique.

2.2. Preparation of $ReOCl_3(O^{\cap}NH)(PPh_3)$

A mixture of 0.50 g (0.60 mmol) of ReOCl₃(PPh₃)₂ and 0.23 g (1.24 mmol) of 2-(diethylaminomethyl)-4methylphenol in toluene (40 ml) was heated at 65°C for 30 min. Triethylamine (0.2 ml) was then added and the mixture was kept at 65°C for a further 30 min. The green precipitate was filtered, washed with ethanol and ether, and finally dried in vacuo. Yield: 53% (0.24 g). Anal. Calc. for C₃₀H₃₄Cl₃NO₂PRe: C, 47.15; H, 4.48; N, 1.83; P, 4.05; Re, 24.37. Found: C, 47.34; H, 4.31; N, 1.74; P, 3.95; Re, 24.08%. IR (cm^{-1} , KBr): 982, v(Re=O); 1286, v(C-ORe). Mass spectrum (FAB⁺): $[M]^+$ 763; $[M - Cl]^+$ 728; $[M - L - Cl]^+$ 535. ³¹P{¹H} NMR (ppm, CDCl₃, 161.98 MHz): -12.0 (s). ¹H NMR (ppm, CDCl₃, 400 MHz) (see atom labelling in Scheme 1): 1.30 (t, 6H, N(CH₂CH₃)₂); 2.06 (s, 3H, CH₃Ph); 2.87 (h, 2H, N(CH_aH_bCH₃)₂, ${}^{2}J(H_{a}-H_{b}) \sim 14$ Hz, ${}^{3}J(H_{a}-H_{N}) \sim 7$ Hz, ${}^{3}J(H_{a}-H_{Me}) \sim 7$ Hz); 3.32 (m, 2H, N(CH_a $H_{\rm b}$ CH₃)₂); 3.64 (d, 2H, Ph–CH₂–N, ${}^{3}J$ (H– H_N = 6.3 Hz); 6.50 (s, 1H, H₃); 6.32, 6.58 (d, 1H each, H_5 , H_6 , ${}^{3}J = 8.4$ Hz,); 7.23–7.80 (m, 15H, PPh₃); 8.15 (s, br, 1H, H_N).

2.3. X-ray diffraction

Single crystals were obtained by slow crystallisation in CH₂Cl₂-ether at 20°C. The experiment was carried out with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatised Cu K α radiation ($\lambda =$ 1.54056 Å). The reduced cell was deduced from 25 reflections detected on a rotation photograph. The Niggli parameters ruled out non-primitive lattices. The monoclinic Laue symmetry and systematic absences checked on the full data set unambiguously defined space group $P2_1/c$. Crystallographic data are summarised in Table 1.

The intensities were collected by the $\omega/2\theta$ scan technique. Orientation and intensity were checked every hour with five standards. A whole sphere of data (20637 reflections) was collected. Intensity fluctuation remained within +2.1% during data collection. The data were corrected for absorption (Gaussian integration, NCRVAX [12], transmission range 0.13–0.64). Equivalent reflections were averaged and the corrections for the effects of Lorentz and polarisation were applied. The final data set consisted of 5693 independent reflections, of which 4420 with $I > 2.0\sigma(I)$ were retained for structure determination. The structure was solved by the direct methods of SHELXS-86 [13] and ΔF syntheses. Refinement was carried out on F^2 with SHELXL-93 [14]. All non-hydrogen atoms were refined anisotropically. Phenyl and methylene hydrogens were

introduced at idealised positions. The methyl group orientations and N–H proton position were determined from a ΔF map. All hydrogen atoms were allowed to ride on their respective non-hydrogen atom, and their isotropic temperature factor was adjusted to 50% (methyl) or 20% (others) above the U_{iso} factor of this atom. Refinement converged to a conventional *R* factor of 0.0295. The general background in the final ΔF map was within ± 0.40 e Å⁻³, whereas the highest peak and deepest valley (near Re) were 1.05 and -0.77 e Å⁻³, respectively.

3. Results and discussion

3.1. Reactivity

2 - (Diethylaminomethyl) - 4 - methylphenol (N O OH) and ReOCl₃(PPh₃)₂ were heated for 30 min in toluene at 65°C, whereupon ligand exchange took place according to Eq. (1).

$$ReOCl_{3}(PPh_{3})_{2} + N^{\circ}OH$$

$$\rightarrow ReOCl_{3}(O^{\circ}NH)(PPh_{3}) (1) + PPh_{3}$$
(1)

The green precipitate is readily soluble in CH_2Cl_2 and $CHCl_3$, but nearly insoluble in Et_2O , EtOH, toluene, acetonitrile and hydrocarbons. It is stable as a solid as well as in solution, and deprotonation is never observed, even when NEt_3 or the very strong bases NaH or KOBu^t are added during the synthesis.

Elemental analysis and fast atom bombardment mass spectroscopy (FAB⁺) agree with the formula ReOCl₃-(O N H)(PPh₃). The molecular ion peak is observed at 763.

3.2. X-ray diffraction study

A crystallographic study was undertaken to determine the ligand binding mode and the stereochemistry around the metal. The ORTEP drawing of the molecule is shown in Fig. 1. Selected bond distances and angles are listed in Table 2.

The crystal contains monomeric molecules in which the octahedral coordination around the metal includes the oxo group, the PPh₃ ligand and three Cl atoms adopting a *mer* arrangement. The phenolate oxygen occupies the sixth coordination site, *trans* to the oxo group, in agreement with the marked preference of oxo-rhenium(V) compounds with oxygen donor ligands for a *trans*-O=Re-O configuration [15]. The aminophenol does not act as a bidentate ligand as previously observed [2–5], but as a monodentate phenolate in which the *ortho* side-arm plays the role of proton quencher. This zwitterionic species is stabilised by an



Fig. 1. ORTEP drawing of the $ReOCl_3(O^{NH})(PPh_3)$ molecule. Ellipsoids correspond to 40% probability. Hydrogens are omitted for clarity, except for that of the ammonium group, which forms a hydrogen bond (thin line) with Cl(1).

intramolecular N-H…Cl hydrogen bond involving the ammonium group.

To our knowledge, crystallographic results are available for only four other oxo–Re(V) compounds of the ReO₂Cl₃P type. In all cases, the arrangement of the donor atoms is the same as observed here. Three are neutral and contain a carbonyl-like donor: ReOCl₃-(PPh₃)(DMF) [16], ReOCl₃(PhEt₂P)(PhEt₂P=O) [17] and ReOCl₃(Ph₂P–CH₂–P(=O)Ph₂) [18,19]. The fourth compound, [ReOCl₃{(OC₆H₄)PPh₂}]⁻, is the most closely related to the present system, since it is anionic and its coordination sphere includes a phosphine and phenolate oxygen [20].

Departure from idealised octahedral angles in compound 1 originates mainly from the widespread tendency of the Re=O group to repel the adjacent metal-ligand bonds. However, in the $\text{ReO}_2\text{Cl}_3\text{P}$ structures known, only the Re–Cl bonds are affected. The effect remains small in 1 (O–Re–Cl = 93.3–95.4°) compared with the above compounds, where at least one

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

Re–O(1)	1.915(3)	Re-O(2)	1.669(3)
Re-Cl(1)	2.449(1)	Re-Cl(2)	2.421(1)
Re–Cl(3)	2.396(1)	Re–P	2.471(1)
O(1)–C(1)	1.353(5)		
O(1)-Re-O(2)	178.2(2)	O(2)–Re–P	88.6(1)
O(1)-Re- $Cl(1)$	86.1(1)	Cl(1)-Re- $Cl(2)$	87.61(4)
O(1)-Re- $Cl(2)$	85.7(1)	Cl(1)-Re- $Cl(3)$	87.30(5)
O(1)-Re- $Cl(3)$	87.5(1)	Cl(1)–Re–P	174.57(4)
O(1)–Re–P	89.8(1)	Cl(2)-Re-Cl(3)	171.78(4)
O(2)-Re- $Cl(1)$	95.4(1)	Cl(2)–Re–P	88.50(4)
O(2)-Re- $Cl(2)$	93.3(1)	Cl(3)–Re–P	96.12(4)
O(2)-Re-Cl(3)	93.6(1)	Re–O(1)–C(1)	166.0(3)

angle is greater than 99.9° (O=Re–Cl = $92.7-106.5^{\circ}$, mean = 98.8°). In contrast, the Re–P bond is displaced slightly towards the Re=O bond: the O(2)–Re–P angle is $88.6(1)^{\circ}$ in 1 and in the $86.7-87.5^{\circ}$ range for the remaining compounds. This pattern seems to be typical of phosphines, independent of whether the phosphine is monodentate or chelating.

The most remarkable feature of 1 concerns the phenolate ligand: it is approximately end-on coordinated $(\text{Re-O-C} = 166.0(3)^\circ)$ and it forms a Re-O bond (1.915(3) Å) much shorter than those observed for $[ReOCl_3{(OC_6H_4)PPh_2}]^-$ (2.016(6) Å) [20] and other compounds with the same P^{O} ligand [8,20,21]. Considering that a Re–O–C angle of $\sim 127^{\circ}$ is imposed by the chelate ring in the latter case, it would be tempting to ascribe this large increase in bond length to a change of the hybridisation state of oxygen from sp to approximately sp². However, the structure of the ReO(OPh)₂- (pz_4B) complex, where pz_4B^- is a tridentate tetrakis-(pyrazolyl)borate ligand [22], suggests that this effect should not be so large, since Re-O distances of 1.946(5) and 1.963(5) Å are found for phenolate ligands, which make Re-O-C angles of 125.9(4) and 127.5(4)°, respectively. Therefore, hybridisation may play a role, but other constraints introduced by the chelate ring, including intramolecular non-bonded contacts and distortion in the coordination polyhedron (for instance, the O=Re-O angle is 163.6(3)°), also undoubtedly contribute to making the Re-O bond longer in the chelates.

The remaining bonds to rhenium are more conventional. The Re=O distance (1.669(3) Å) is shorter than for ReO(OR)Cl₂(PPh₃)₂ and related compounds [25], but apparently normal for a ReO₂Cl₃P complex of this type, since the same value was obtained for [ReOCl₃- $\{(OC_6H_4)PPh_2\}]^-$ [20]. The Re–P bond in 1 (2.471(1) Å) is longer than in the latter compound (2.422(2) Å), but such a difference is normal for this pair of ligands. The chelate compound shows Re-Cl bonds systematically shorter than in 1. For instance, the mutually trans Re–Cl(2) and Re–Cl(3) bonds (2.421(1) and 2.396(1) Å) in 1, although in the normal range for mono-oxo compounds [25], are significantly longer than those of $[\text{ReOCl}_3\{(\text{OC}_6\text{H}_4)\text{PPh}_2\}]^-$ (2.398(3) and 2.374(3) Å). Probably because the small angle $(76.1(2)^\circ)$ in the chelate ring leaves more room around the metal for the remaining ligands in the latter case. The Re-Cl(1) bond in 1, trans to P, is particularly long (2.449(1) Å versus 2.369(2) Å in the chelate): this is consistent with the strong *trans* influence of phosphines. The N-H…Cl hydrogen bond does not deviate much from linearity $(N-H-Cl = 158^{\circ})$, but the N–Cl separation (3.318(5) Å) is somewhat greater than the typical value of 3.21 Å proposed for this type of bond [23].

The phosphine adopts the common propeller conformation (Re–P–Cn1–C_{ortho} angles = 45.6(4), 61.6(4) and 51.9(4)° for n = 1, 2 and 3, respectively) and its P–C(21)

bond is approximately eclipsed with the Re–Cl(3) bond (Cl(3)–Re–P–C(21) = $-5.7(2)^{\circ}$). The phenyl ring of the phenolate unit is roughly coplanar with the ReOCl₃ plane (dihedral angle of 19°), thereby preventing short contacts with the phenyl rings of PPh₃.

3.3. Spectroscopic results

The IR spectrum displays a strong absorption at 982 cm⁻¹ assigned to v(Re=O). Three medium bands in the same region (932, 946 and 970 cm⁻¹) correspond to v(N-C) vibrations [24]. The v(C-ORe) frequency of the coordinated phenolate group is detected as a strong band at 1286 cm⁻¹, shifted by + 27 cm⁻¹ from the free ligand position. These frequencies correspond with those observed in the Ni and Cu complexes [2,4]. The v(N-H) vibration is likely responsible for a medium, relatively sharp, band at 3062 cm⁻¹, including various weaker C–H features in the low wavenumber wing.

The solid-state structure is retained in solution, as evidenced from the ¹H NMR data. The spectrum of **1** at r.t. exhibits a clear signal at 8.15 ppm for the N-H proton. The aromatic ring gives, as expected, a singlet at 6.50 ppm for H3 (Scheme 1), doublets at 6.32 and 6.58 ppm for the coupled H5 and H6 protons, and a singlet at 2.06 ppm for the 4-methyl group. The usual multiplet is observed at 7.2-7.8 ppm for PPh₃. The remaining resonances were assigned by comparison with those of related Zn compounds [2,3]. Even though the α -CH₂ protons are inequivalent under static conditions in the crystal, they give an averaged signal at 3.64 ppm because of fast motion in solution. It should be noted, however, that instead of the singlet expected, a doublet is obtained due to coupling with the N-H proton (${}^{3}J = 6.3$ Hz), which indicates that the latter proton is not labile on the NMR time scale. The two ethyl groups are also averaged in solution. The ethyl CH₂ protons are inequivalent and give individual resonances, being connected to a N atom bearing three different substituents. The multiplet at 2.87 ppm (H_a) actually contains seven components as a result of couplings with the geminal H_b proton (²J ~ 14 Hz), the three methyl protons H_{Me} (${}^{3}J \sim 7$ Hz) and the H_{N} proton (${}^{3}J \sim 7$ Hz). A multiplet is found for the second ethyl CH₂ proton at 3.32 ppm, but it is not so well resolved. As mentioned previously for Zn complexes [3], the high-field signal likely corresponds to the proton closer to the coordinated Cl atoms. The terminal methyl groups appear as a pseudo-triplet, indicating equal coupling constants with the two adjacent CH₂ protons.

4. Conclusion

In contrast with the related $P \cap OH$ ligands, which form chelates with the Re(V) oxo core, the present $N \cap OH$ molecule binds in a monodentate manner via the deprotonated phenolate group, the amino group acting as proton quencher. This difference observed between the two types of ligands originates from the relative affinities of the protons and Re center for amine and phosphine donors, the amino group being more reactive towards the electrophilic proton than toward the rhenium centre, whereas the opposite trend applies to phosphorus.

The complex described in this paper results from selective ligand exchange leading to the substitution of one PPh₃ by a phenolate ligand. Under similar reaction conditions, $[ReOCl_4]^-$ gave several reactive species, which could not be separated and isolated. On the other hand, no reaction was observed to take place with ReNCl₂(PPh₃)₂.

The orientation of the phenolate group in the complex raises interesting questions about the electronic structure. In a linear O=Re-O-R unit, the alkoxide oxygen possesses p orbitals available to interact with the rhenium d orbitals and generate a delocalised π -system. Generally, this factor does not seem to introduce huge stabilisation in simple $ReO(OR)Cl_2L_2$ molecules (R = Me, Et, i-Pr; L = PPh₃) N-heterocycle) [25], since the Re–O–R angle is usually near 145°, although angles $> 168^\circ$ were found in two cases. The effect may be more important in the present case, since delocalisation could extend over the phenyl ring. Partial multiple character in the Re-O(2) bond would be consistent with this bond being ~ 0.04 Å shorter than in ReO(OPh)₂(pz₄B) [22], where conjugation is impossible since the PhO⁻ ligand is *cis* to the Re-O bond. However, the remaining ligands being very different in these two compounds, a larger sample of structures is needed to reliably assess the role of π -bonding. It should be noted that the amino-phenol ligand used in this study could be a valuable tool for investigating this point, since its protonated side-arm helps freezing in the end-on configuration, a phenolate ligand that could otherwise coordinate with a bent orientation.

5. Supplementary material

Lists of atomic coordinates and thermal parameters, distances, bond angles, torsion angles and least-squares planes for the crystal structure are available upon request.

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