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Note

Synthesis and characterization of a binuclear rhenium nitropyrazole complex $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$

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Abstract

The binuclear nitropyrazole compound $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$ (**3**) was synthesized by refluxing $[ReOCl_2(OEt)(PPh_3)_2]$ and 2-nitropyrazole in ethanol for 12 h. The octahedral $\{ReO_2N_2ClP\}$ sites are linked by two bridging nitropyrazoles and an oxo group, with an Re–O–Re angle of 124.7(6)°. Compound **3** is electrochemically active, displaying a reversible one electron reduction at −0.55 V with respect to Ag/Ag^+. Crystal data: $C_{36}H_{34}Cl_2N_6O_7P_2Re_2$ (**3**), monoclinic $C2/c$, $a=32.569(7)$, $b=9.624(2)$, $c=29.151(6)$ Å, $\beta=109.33(3)°$, $V=8622(3)$ Å^3, $Z=8$, $D_{calc}=1.799$ g cm^{-3}, structure solution and refinement based on 3364 reflections converged at $R=0.056$.

Keywords: Crystal structures; Rhenium complexes; Nitropyrazole complexes; Binuclear complexes

1. Introduction

Recently there has been expanded interest in metal-based nitroimidazole-related compounds [1–4]. The importance of these compounds is demonstrated by their ability to mark hypoxic (oxygen deficient) cell regions and radiosensitize tumor cells [5,6]. Such hypoxic regions are characteristic of solid tumors, which often contain poorly oxygenated regions due to the rapid cell growth that outpaces the developing blood vessels, causing the reduction of the supply of nutrients to the cells, particularly oxygen. The slow metabolism of the nitro compounds and their ability to diffuse through nonvascular cell masses allow deep penetration, making them effective tools for marking the hypoxic cells present in the tumor. Radiosensitization refers to the enhancement of radiation induced therapy with certain drugs [7], a requirement for tumors containing hypoxic regions as these cells are resistant to radiotherapy. Since the role of the radiosensitizers is to act similarly to dioxygen in these hypoxic regions, the electron affinic nitro group is an essential component that allows drugs requiring dioxygen to be more effective [8].

We are interested in the synthesis of new rhenium containing organo-nitro compounds for the potential treatment of cancer induced hypoxia. By complexing these organo-nitro ligands to Tc and Re, there exists the possibility to image and treat these hypoxic regions with the appropriate radionuclide [9,10]. Previously reported Pt(II) and Rh(II) nitroimidazole and related compounds have shown some success in these applications [11,12]. In this study, we report the synthesis and characterization of a binuclear rhenium nitropyrazole species, $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$.

2. Experimental

2.1. General considerations

NMR spectra were recorded on a General Electric QE 300 (^{1}H 300.10 MHz) spectrometer in CD_2Cl_2 (δ 5.32), D_2O (δ 4.75). IR spectra were recorded as KBr pellets with a Perkin-Elmer Series 1600 FTIR. Electrochemical experiments were performed by using a BAS CV-27 Cyclic Voltammograph and a Bas Model RXY recorder. A three-compartment, gas-adapted cell was used with a glassy carbon working electrode, a platinum wire auxiliary electrode and a silver/silver chloride reference electrode. Cyclic voltammograms were recorded under N_2 in dry DMF which was 0.2 M in supporting electrolyte (tetrabutylammonium hexafluorophosphate [TBAP]) and sufficient sample for reasonable current observations. Elemental analysis for carbon, hydrogen and nitrogen was carried out by Oneida Research Services, Whitesboro, NY.

All synthetic manipulations were carried out open to the atmosphere. All solvents were of reagent grade and were used

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as received. Ammonium perrhenate and pyrazole were purchased from Aldrich chemical and used as received.

2.2. Syntheses

2.2.1. Preparation of $C_3H_3N_3O_2$ (1)

All steps were performed open to the atmosphere. In a 100 ml Schlenk flask placed in an ice–water bath was mixed pyrazole (10.0 g, 147.0 mmol), 95% H_2SO_4 (20 ml) and concentrated HNO_3 (20 ml). Concentrated H_2SO_4 (40 ml) was added to the reaction mixture. The reaction was stirred and heated at 110°C for 2 days. The solution was poured into 400 ml of ice–water forcing the product **1** to precipitate as a white solid, which was collected by filtration and washed with 1.0 l distilled H_2O. The filtrate was neutralized to pH 7.0 with $NaOH/NaHCO_3$, yielding more precipitate (10.7 g, 64%). IR (KBr pellet, cm^{-1}): 3176 (s), 3133 (s), 2890 (m), 1505 (s), 1410 (s), 1358 (s), 1288 (s), 1190 (m), 1159 (m), 1029 (m), 997 (s), 938 (s), 893 (m), 850 (m), 817 (s), 755 (s), 592 (s), 546 (s). ^1H NMR (D_2O, 295 K): δ (8.37 s, 2H). Cyclic voltammetry ($E_{1/2}$, DMF): -1.086 V, -2.066 V ($\Delta E_p = 159$ mV).

2.2.2. Preparation of $[ReOCl_2(OEt)(PPh_3)_2]$ (2)

All steps were performed open to the atmosphere. To a solution of PPh_3 (5 g, 19 mmol) in EtOH (30 ml) was added a solution of 37% HCl (3.5 ml, 30 mmol) containing NH_4ReO_4 (1 g, 3.73 mmol). The solution was refluxed in a 50 ml schlenk flask for 10 min, whereupon the color of the solution changed from milky white to olive. The reaction was cooled to room temperature and filtered. The precipitate was washed with two 10 ml portions of EtOH and two portions of Et_2O to yield $[ReOCl_2(OEt)(PPh_3)_2]$ in quantitative yield (3 g) [13].

2.2.3. Preparation of $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$ (3)

2.2.3.1. Method 1

All steps were performed open to the atmosphere. In a 50 ml schlenk flask, NH_4ReO_4 (0.05 g, 0.186 mmol), 2-nitropyrazole (0.083 g, 0.746 mmol), and PPh_3 (0.098 g, 0.372 mmol) were added in 10 ml methanol containing 37% HCl (0.275 g, 7.463 mmol). The reaction was refluxed for 2 h. The green product **3** was collected by filtration (0.055 g, 24%)

2.2.3.2. Method 2

All steps were performed open to the atmosphere. In a 50 ml Schlenk flask, $[ReOCl_2(OEt)(PPh_3)_2]$ (0.20 g, 0.241 mmol) was added to 2-nitropyrazole (0.113 g, 0.990 mmol) in ethanol (25 ml). The reaction was refluxed overnight. The green product **3** was collected by filtration (0.12 g, 39%). A small sample was dissolved in CH_2Cl_2 and layered with pentane to yield dark green crystals. *Anal*. Calc. for $C_{42}H_{34}N_6O_7Re_2Cl_2P_2$ (mol. wt. 1239.68): C, 40.7; H, 2.74; N, 6.77. Found: C, 40.7; H, 2.61; N, 6.94. IR (KBr pellet, cm^{-1}): 1508 (s), 1435 (m), 1406 (m), 1294 (s), 1189 (w), 1096 (m), 1046 (m), 999 (w), 972 (m), 867 (w), 818 (m), 748 (s), 710 (m), 693 (s), 629 (s), 526 (s). ^1H NMR (CD_2Cl_2, 295 K, δ (ppm)): 7.20 (s), 7.34 (m), 7.46 (m), 8.03 (s). Cyclic voltammmetry ($E_{1/2}$, DMF): -0.547 V ($\Delta E_p = 61$ mV).

Table 1
Summary of crystal data for the structure of $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$ (**3**)

Formula	$C_{42}H_{34}Cl_2N_6O_7P_2Re_2$
Formula weight	1240.0
a (Å)	32.569(7)
b (Å)	9.624(2)
c (Å)	29.151(6)
β (°)	109.33(3)
V (Å^3)	8622(3)
Z	8
D_{calc} (g cm^{-3})	1.910
Space group	$C2/c$
Absorption coefficient (Mo Kα) (mm^{-1})	5.940
No. of reflections ($F > 6.00\sigma(F)$)	3364
R [a]	0.0560
Rw [b]	0.0786

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

2.3. X-ray crystallography

Compound **3** was studied using a Rigaku AFC5S diffractometer, equipped with a low temperature device. To minimize crystal degradation, data collection was collected at 253 K. Crystal stability was monitored using 3 intense reflections in each case and no significant changes in the intensities of these standards were observed over the course of the data collection. An empirical absorption correction based on psi scans was applied to the data, resulting in transmission factors ranging from 0.72 to 1.00. The data was corrected for Lorentz and polarization affects. The structure was solved by the Patterson method. All calculations were performed using the SHELXTL crystallographic software package [14], as described previously [15]. Due to the relatively low data to parameter ratio, the phenyl groups were treated as idealized rings. The crystal parameters and other experimental details of the data collection are summarized in Table 1. Atomic positional parameters are listed in Table 2 and bond lengths and angles in Table 3. A complete description of the details of the crystallographic methods is given in the supplementary materials. An ORTEP view of **3** is presented in Fig. 1 and a schematic view of the bridge geometry in Fig. 2.

3. Results and discussion

3.1. Synthesis and chemical properties

The 2-nitropyrazole was prepared in moderate yield by heating pyrazole in a combination of H_2SO_4 and HNO_3 for

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients [a] ($\text{Å} \times 10^3$)

Re(1)	903(1)	1638(1)	1537(1)	26(1)
Re(2)	1068(1)	3749(1)	663(1)	31(1)
Cl(1)	1418(2)	−159(7)	1786(2)	48(3)
Cl(2)	1366(3)	5914(7)	973(3)	64(4)
P(1)	1166(2)	2763(7)	2346(2)	37(3)
P(2)	1747(2)	3085(7)	513(2)	36(3)
O(1)	1262(4)	2811(14)	1299(5)	24(6)
O(2)	473(5)	884(16)	1643(5)	39(7)
O(3)	799(5)	4158(16)	67(5)	38(7)
O(4)	−378(7)	7071(21)	950(7)	69(10)
O(5)	−578(7)	5461(24)	1352(9)	90(12)
O(6)	377(6)	−1121(19)	−646(6)	62(9)
O(7)	298(6)	−2507(18)	−89(6)	58(8)
N(1)	462(6)	3285(19)	1242(7)	32(5)
N(2)	550(5)	4211(16)	913(6)	19(4)
N(3)	−350(8)	5887(26)	1129(9)	57(6)
N(4)	748(5)	854(17)	821(6)	23(4)
N(5)	785(5)	1740(17)	464(6)	24(4)
N(6)	390(7)	−1393(22)	−230(8)	46(6)
C(1)	118(7)	3797(23)	1335(8)	36(6)
C(2)	−21(7)	4993(23)	1084(8)	32(6)
C(3)	268(8)	5202(26)	835(9)	45(7)
C(4)	597(7)	−361(24)	628(8)	33(6)
C(5)	532(7)	−295(23)	137(8)	30(6)
C(6)	662(7)	1055(23)	55(8)	32(6)
C(7)	1848(8)	4210(25)	54(9)	41(6)
C(8)	1521(8)	4402(26)	−386(9)	45(7)
C(9)	1585(8)	5278(26)	−742(10)	49(7)
C(10)	1978(10)	5897(34)	−633(12)	77(10)
C(11)	2285(9)	5768(29)	−226(10)	58(8)
C(12)	2234(9)	4943(27)	138(10)	52(7)
C(13)	1711(7)	1322(22)	285(8)	27(5)
C(14)	1631(8)	960(27)	−210(9)	47(7)
C(15)	1556(8)	−452(28)	−334(10)	54(7)
C(16)	1547(8)	−1466(28)	−1(9)	49(7)
C(17)	1623(8)	−1049(26)	461(9)	46(7)
C(18)	1695(8)	301(26)	620(10)	47(7)
C(19)	2251(9)	3074(27)	1023(10)	49(7)
C(20)	2623(9)	2401(31)	997(11)	64(8)
C(21)	3005(10)	2424(30)	1373(11)	65(9)
C(22)	3041(11)	2997(34)	1829(13)	82(10)
C(23)	2672(12)	3556(38)	1858(15)	100(12)
C(24)	2281(12)	3652(35)	1488(13)	88(11)
C(26)	2041(8)	2021(25)	2529(9)	73(18)
C(27)	2487	2075	2784	67(17)
C(28)	2649	3047	3155	19(10)
C(29)	2367	3965	3271	58(16)
C(30)	1921	3911	3015	53(15)
C(25)	1759	2939	2644	43(7)
C(32)	865(9)	369(21)	2675(8)	54(15)
C(33)	719	−401	2996	88(22)
C(34)	684	224	3413	66(9)
C(35)	795	1619	3510	76(19)
C(36)	942	2388	3189	37(12)
C(31)	977	1764	2772	32(6)
C(38)	597(9)	4802(28)	2500(10)	63(17)
C(39)	391	6092	2406	81(20)
C(40)	524	7081	2134	93(23)
C(41)	862	6779	1956	69(9)
C(42)	1068	5488	2051	53(7)
C(37)	936	4500	2323	71(9)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å) and angles (°)

Re(1)–Cl(1)	2.352 (6)	Re(1)–P(1)	2.477 (6)
Re(1)–O(1)	1.912 (15)	Re(1)–O(2)	1.696 (17)
Re(1)–N(1)	2.120 (17)	Re(1)–N(4)	2.116 (17)
Re(2)–Cl(2)	2.350 (7)	Re(2)–P(2)	2.476 (8)
Re(2)–O(1)	1.969 (14)	Re(2)–O(3)	1.713 (14)
Re(2)–N(2)	2.093 (18)	Re(2)–N(5)	2.138 (16)
P(1)–C(25)	1.844 (24)	P(1)–C(31)	1.832 (27)
P(1)–C(37)	1.824 (28)	P(2)–C(7)	1.834 (28)
P(2)–C(13)	1.812 (22)	P(2)–C(19)	1.815 (23)
O(4)–N(3)	1.245 (32)	O(5)–N(3)	1.208 (39)
O(6)–N(6)	1.228 (30)	O(7)–N(6)	1.220 (29)
N(1)–N(2)	1.406 (26)	N(1)–C(1)	1.333 (33)
N(2)–C(3)	1.293 (30)	N(3)–C(2)	1.414 (36)
N(4)–N(5)	1.382 (25)	N(4)–C(4)	1.322 (25)
N(5)–C(6)	1.304 (28)	N(6)–C(5)	1.465 (30)
C(1)–C(2)	1.358 (31)	C(2)–C(3)	1.378 (40)
C(4)–C(5)	1.378 (33)	C(5)–C(6)	1.412 (32)
Cl(1)–Re(1)–P(1)	92.3(2)	Cl(1)–Re(1)–O(1)	94.9(4)
P(1)–Re(1)–O(1)	91.5(4)	Cl(1)–Re(1)–O(2)	100.2(5)
P(1)–Re(1)–O(2)	93.3(5)	O(1)–Re(1)–O(2)	163.9(6)
Cl(1)–Re(1)–N(1)	173.4(6)	P(1)–Re(1)–N(1)	91.9(5)
O(1)–Re(1)–N(1)	79.9(7)	O(2)–Re(1)–N(1)	84.6(7)
Cl(1)–Re(1)–N(4)	87.5(5)	P(1)–Re(1)–N(4)	171.6(5)
O(1)–Re(1)–N(4)	80.2(6)	O(2)–Re(1)–N(4)	95.0(7)
N(1)–Re(1)–N(4)	87.6(7)	Cl(2)–Re(2)–P(2)	91.0(3)
Cl(2)–Re(2)–O(1)	94.7(4)	P(2)–Re(2)–O(1)	91.2(5)
Cl(2)–Re(2)–O(3)	101.2(5)	P(2)–Re(2)–O(3)	93.8(6)
O(1)–Re(2)–O(3)	163.3(6)	Cl(2)–Re(2)–N(2)	87.5(5)
P(2)–Re(2)–N(2)	170.2(4)	O(1)–Re(2)–N(2)	79.4(6)
O(3)–Re(2)–N(2)	95.9(7)	Cl(2)–Re(2)–N(5)	173.1(6)
P(2)–Re(2)–N(5)	92.7(5)	O(1)–Re(2)–N(5)	79.4(6)
O(3)–Re(2)–N(5)	84.4(7)	N(2)–Re(2)–N(5)	87.9(7)
Re(1)–P(1)–C(25)	117.9(9)	Re(1)–P(1)–C(31)	109.2(7)
Re(1)–P(1)–C(37)	110.9(8)	Re(2)–P(2)–C(7)	111.3(8)
Re(2)–P(2)–C(13)	110.7(8)	Re(2)–P(2)–C(19)	118.4(11)
Re(1)–O(1)–Re(2)	124.5(6)	Re(1)–N(1)–N(2)	119.2(14)
Re(1)–N(1)–C(1)	134.1(16)	N(2)–N(1)–C(1)	106.2(17)
Re(2)–N(2)–N(1)	118.1(12)	Re(2)–N(2)–C(3)	134.8(17)
Re(1)–N(4)–N(5)	118.1(12)	Re(1)–N(4)–C(4)	132.0(16)
Re(2)–N(5)–N(4)	119.4(12)	Re(2)–N(5)–C(6)	132.9(16)

two days. The white product was precipitated by pouring the solution into ice–water.

The binuclear complex $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$ (**3**) was obtained in good yield from the rhenium starting material $[ReOCl_2(OEt)(PPh_3)_2]$ and 2-nitropyrazole, which were refluxed 12 h in ethanol in the absence of a deprotonating agent. The product **3** precipitates from this solution as a pale green solid, which was recrystallized by slow diffusion of pentane into a CH_2Cl_2 solution of **3**.

The IR spectrum for **3** does not exhibit strong bands in the 800–1000 cm^{-1} region, assignable to $\nu(Re{=}O)$; however, medium intensity bands do appear at 972 and 818 cm^{-1}. The presence of the ligand is demonstrated by bands at 1508 and 1294 cm^{-1}. The ^1H NMR spectrum at room temperature exhibits a complex aromatic region, while the free ligand gives only one peak at 8.37 ppm.

The electrochemistry of 2-nitropyrazole displays an irreversible reduction at −1.086 V and a reversible reduction at

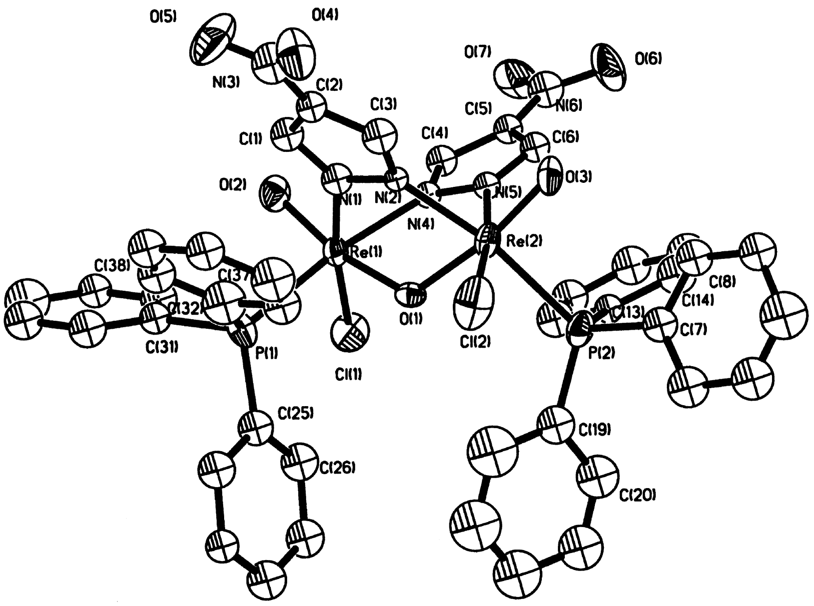

Fig. 1. A view of the structure $[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$ (**3**) showing the atom-labeling scheme.

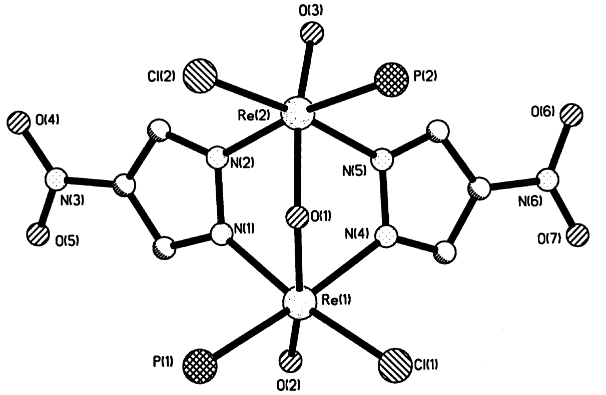

Fig. 2. Schematic representation of the Re-coordination and of the bridge geometry of **3**. The carbon atoms of the Ph_3P groups have been omitted for clarity.

−2.066 V. The reduction process at −1.086 V is typical of other nitro-containing ligands with potential radiosensitizing properties including the substituted nitroimidazoles, fluorinated nitroazoles, and the extensively studied misonidazole [16]. The electrochemistry of **3** exhibits a reversible one-electron reduction at −0.547 V with $\Delta E_p = 61$ mV. The shift to more positive potential observed for the metal-bound pyrazole in **3** compared to the free ligand is not unprecedented [9]. The electrochemistry observed for nitro-containing complexes has been shown to be strongly influenced by solvent, nature of the supporting electrolyte, pH, and concentration. These factors make any direct comparisons between reduction potentials for this class of compounds tenuous at best.

3.2. *Description of structure*

The structure of **3** reveals the presence of two rhenium(V) centers linked through two bridging nitropyrazoles and an oxo group. The familiar $\{Re_2O_3\}$ core has a μ-oxo bridge with a Re–O–Re angle of 124.7(6)°, most probably due to the geometric constraints of the two bridging nitropyrazole ligands. The overall structure of **3** consists of two corner-sharing octahedra with each rhenium having a terminal oxo-group, two nitrogen donors, chlorine donor, the μ-oxo bridge, and the phosphorous donor of a triphenylphosphine defining the coordination sites. The structure resembles a 'butterfly complex' with the two nitropyrazoles as the 'wings'.

The bond lengths and angles observed for the $\{Re_2O_3\}$ core are compared to a variety of binuclear μ-oxo rhenium complexes in Table 4. In compounds bridged only by a single μ-oxo group such as $[Re_2O_3Cl_4(C_5H_5N)_4]$ and $[Re_2O_3(CN)_8]$, the Re–O–Re angle is essentially linear. In contrast the angle decreases as the geometric constraints of other bridging ligands are introduced, as illustrated by $[Re_2O_3(OMe)_6]$, $[Re_2OCl_5(C_2H_5CO_2)(PPh_3)_2]$, and compound **3**. The Re–O distance for the μ-oxo bridge is approximately 1.90–2.00 Å, while rhenium terminal oxo-group distances range from 1.65–1.75 Å, as illustrated by the iodo complexes $[Re_2O_5I_2(PPh_3)_2]$ and $[Re_2O_5I_2(PPh_3)(OPPh_3)]$. The structural diversity of the dimers is reflected by the numerous possible bridging coligands.

As noted, the terminal Re–O lengths in **3** are unexceptional, exhibiting distances of 1.69(2) Å and 1.70(1) Å for Re1 and Re2, respectively. The Re–N distances range from 2.08(2) Å to 2.14(2) Å, which is well within the range of distances observed for other examples of Re(V) complexes, as listed in Table 5.

4. Conclusions

The ease of preparation, high purity, reasonable yield, and the presence of labile chlorine donors in **3** lead us to believe

Table 4
Selected bond distances (Å) and angles (°) for representative oxo-bridged Re complexes [a]

Complex	Re–O$_b$ [b]	Re=O$_t$	Re–O$_b$–Re	X [c]	O$_t$=Re–O$_b$	Ref.
$[Pt(NH_3)_4]_2[Re_2O_3(CN)_8][Re_2O_3(OMe)_6]$	1.9149(4)	1.698(7)	180.0	O	179.5(8)	[17]
	1.917(13)	1.690(11)	83.8(5)	(OMe)	99.4(6)	[18]
	1.916(13)	1.703(12)			99.8(6)	
$[Re_2O_5I_2(PPh_3)_2]$	2.031(6)	1.670(7)	164.3(4)	O	179.9(5)	[19]
	1.797(6)				104.5–117.8	
$[Re_2O_5I_2(PPh_3)(OPPh_3)]$	2.079(9)	1.639(9)	153.5(5)	O	175.9(4)	[19]
	1.78(1)				109.4–111.1	
$[Re_2OCl(C_2H_5CO_2)\{P(C_6H_5)_3\}_2]$	1.896(11)		83.8(5)	Cl		[20]
	1.903(16)	1.764(16)	174.5(9)	O	165.5(7)	[21]
	1.943(16)	1.715(16)			172.8(7)	
$[Re_2O_3Cl_2(PPh_3)_2(C_3H_2N_3O_2)_2]$	1.922(14)	1.688(16)	124.7(6)	O	163.4(6)	This work
	1.955(13)	1.704(13)			163.8(6)	

[a] E.s.d.s in parentheses.
[b] Abbreviations: O$_b$ ≡ bridging oxo-group; O$_t$ ≡ terminal oxo-group.
[c] X ≡ ligand *trans* to bridging oxo-group.

Table 5
Selected bond distances (Å) for representative Re(V)–oxo complexes [a]

Complex	Re=O	Re–Cl	X [b]	Re–P	Y [c]	Ref.
$[ReOCl_2(PPh_3)(acac)]$	1.69(1)	2.376(7)	Cl	2.431(4)	O	[22]
		2.339(7)	Cl			
$[Re_2O_2Cl_4(PPh_3)(salen)]$	1.68(1)	2.367(3)	N	2.466(4)	Cl	[23]
	1.68(1)	2.365(3)	N	2.472(4)	Cl	
$[ReOCl_2(PPh_3)\{Ph(O)–CNNCMe_3\}]$	1.685(8)	2.344(4)	N	2.472(2)	Cl	[24]
		2.388(3)	P			
trans-$[ReOCl_2(PPh_3)(Me–sal)]$	1.701(5)	2.375(2)	Cl	2.471(2)	N	[25]
		2.430(2)	Cl			
cis-$[ReOCl_2(PPh_3)(Me–sal)]$	1.660(8)	2.355(3)	N	2.485(3)	Cl	[25]
		2.397(3)	P			
trans-$[ReOCl_3(PEt_2Ph)_2]$	1.60	2.41	Cl	2.45	P	[26]
		2.47	O	2.48		
		2.43	Cl			
$[Re_2OCl_5(C_2H_5CO_2)(PPh_3)_2]$		2.318(4)	O	2.474(4)	Cl	[20]
		2.302(5)	O	2.506(4)	Cl	
		2.340(5)	O			
		2.371(5)	O			
$[Re_2O_3Cl_2(PPh_3)(C_3H_2N_3O_2)_2]$	1.688(16)	2.349(6)	N	2.476(6)	N	This work
	1.704(13)	2.350(6)	N	2.475(7)	N	

[a] E.s.d.s in parentheses.
[b] X ≡ donor group *trans* to Cl.
[c] Y ≡ donor group *trans* to P.

that **3** is a useful binuclear rhenium starting material in developing a system of rhenium organo-nitro derivatives for medicinal applications. The potential for exploiting ^{186}Re and ^{188}Re in nuclear medical applications is particularly attractive in view of its half-life (90 h) and strong β emission (βmax. = 1070 keV), which enable this isotope to deliver high radiation doses to tissues [27]. The chlorine ligands should allow for facile substitution to occur, although early attempts to crystallize derivatives have been unsuccessful to date. Ligand substitution for chlorine provides the means to study influence of coligands on the electrochemical behavior and biodistribution patterns of the derivatives [28].

We have successfully incorporated a nitropyrazole into a Group 7 transition metal complex whereas all previous examples employ later transition elements [29,30]. This may allow for the development of early transition element hypoxic marker derivatives. Moreover, the combination of a radiosensitizing agent plus a radioactive element in the same molecule could allow for improved hypoxic tumor treatment.

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